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MATHEMATICAL TABLES

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RESEARCH PAPER RP1415

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A PHYSICAL PHOTOMETER

By Ray P. Teele

ABSTRACT

The unreliable and differing characteristics of observers' eyes have prevented photometry from being an exact science. A physical photometer has been constructed, consisting of a thermopile, a potentiometer, and a filter which has at each wavelength a transmission proportional to the ICI luminosity factor for that wavelength. This photometer gives results which are consistent with the ICI luminosity factors and which are more accurate than those obtained by visual observers when the photometric fields are not color-matched.

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1. INTRODUCTION

Photometry has been carried on for many years by means of visual observations, not because the eye is an accurate measuring instrument but because there has been no physical apparatus which would respond to radiant energy in the same manner as the human eye with an accuracy comparable with that of visual observations made under the best conditions.

Vision is a combined physiological and psychological process. In the visual photometry of colored lights, otherwise normal observers may obtain markedly differing positions of photometric balance because of their differing brightness evaluations of different parts of the spectrum.

Experience shows not only that the results obtained in heterochromatic photometry are influenced by the characteristics of the eye of the observer, but also that nearly all observers using the equality-of-brightness method will change their decision as to a photometric balance over a period of a month or more. Some observers even exhibit a variation in this decision during a single day.

Even in homochromatic photometry the results obtained are influenced by the attitude of the observer and by his ocular and bodily fatigue or discomfort, and the immediate prior use of an observer's eye must be controlled before observations are made; for example, an observer entering a photometric laboratory from a brightly lighted room requires a period of time to become properly adapted to the light conditions of the photometer room. All of these variations make it desirable to devise a physical instrument to evaluate light.

Various experimenters have worked on the problem. It is sufficient here to note the experiments of Ives and Kingsbury, and of Ives,[1] in 1915, in which a luminosity filter and a thermopile were employed. The luminosity "filter" in one case was a template which was placed in the path of the radiant energy dispersed by a prism. The optical system required and the mechanical difficulties encountered in constructing, mounting, and alining a template has made this method impractical. In the other case the luminosity filter consisted of a liquid solution. In both cases a Thomson galvanometer was used. The susceptibility of this galvanometer to mechanical disturbances and drift of zero, and the lack of exact proportionality between current and deflection in the circuit, imposed serious limitations on their measurements. In order to avoid the difficulties which Ives and Kingsbury encountered, which are present even with the best of modern galvanometers, it was decided in the present work to measure the emf developed, instead of drawing and measuring current from the thermopile. Since this emf is small, it was necessary to develop a special potentiometer and procedure in order to make the measurements to the required accuracy, and these have been described in a previous paper.[2] The present paper gives a more complete description of the physical photometer which was constructed and describes the method of operation and the results of tests which were made to determine its performance.

II. THE PHYSICAL PHOTOMETER

The most fundamental concept in photometry is that of luminous flux. Luminous flux is the rate of passage of radiant energy evaluated by reference to the luminous sensation produced by it. If we have a source emitting equal amounts of radiant energy per unit wavelength throughout the visible spectrum (called an equal-energy spectrum) and have observers evaluate the brightness of this energy at each wavelength, we find that the human eye is not equally responsive to radiant energy throughout the visible spectrum. We find two things: (1) all normal observers find the region of greatest luminosity to be in the yellow-green part of the spectrum, the luminosity gradually decreasing in either direction; but (2) there are important differences in the spectral luminosity curves for different normal observers, which result in their different evaluations of the brightnesses of colored lights. The average spectral luminosity curve of the eye at different wavelengths has been determined for a large number of observers, and an average set of relative values has been accepted by the International Commis-

[1] H. E. Ives and E. F. Kingsbury, Phys. Rev. **6**, 319 (1915).
H. E. Ives, Phys. Rev. **6**, 334 (1915).
[2] R. P. Teele and S. Schuhmann, J. Research NBS **22**, 4 (1939) RP1195.

sion on Illumination as a definition of a "standard" photometric observer.[3] The luminosity curve showing the response of this ideal standard observer for energy received at different wavelengths is given as a solid line in figure 1.

No physical detector has been constructed which has the same relative response curve as the average human eye for radiant energy of different wavelengths. It is possible, however, to make a nonselective receiver, which indicates the amount of received energy per unit time independent of its wavelength. In order to have this nonselective receiver give the same luminous response as the eye of the "standard" observer, it is necessary to interpose between the source and receiver a filter which has at each wavelength a transmission proportional to the luminosity factor for that wavelength. Such a luminosity filter, together with a nonselective receiver and an indicator or measuring device attached to the receiver, constitutes a physical photometer which will measure the rate of passage of radiant energy evaluated by reference to the luminous sensation produced by it, that is, will "see" radiant energy in the same manner as the eye of the standard ICI observer.

1. LUMINOSITY FILTER

The luminosity filter first realized [4] for use as part of the physical photometer was found to lack satisfactory reproducibility, and a second filter,[5] which tests indicate is sufficiently reproducible, was devised. The extent to which the relative transmission of the second luminosity filter duplicates the accepted ICI luminosity curve in the wavelength interval from 380 to 770 mμ is shown in figure 1. The solid line is the ICI luminosity curve, and the plotted points are the transmissions obtained from spectrophotometric data for the luminosity filter. A slight amount of radiant energy is also transmitted by this filter in the infrared region from 800 to 1,320 mμ. The method of correcting for this unwanted band of transmitted energy is discussed in section III.

The filter consists of a piece of glass used in conjunction with a liquid solution. The glass used is a Corning uranium (canary) glass of such a thickness as will give a transmission at 486 mμ of 0.40 $\pm$0.01. The solution has the following composition:

Copper sulfate, $CuSO_4.5H_2O$	20.00	grams
Cobalt ammonium sulfate, $CoSO_4(NH_4)_2SO_4.6H_2O$	2.05	grams
Potassium dichromate, $K_2Cr_2O_7$	0.150	grams
Sulfuric acid, H_2SO_4 (1.835 sp gr)	10	ml
Distilled water to make 1 liter of solution.		

The solution must be used in a cell of 5.00-cm length, which should be placed between the illuminant and the uranium glass (to reduce fluorescence of the latter). Further details regarding the luminosity filter will be published separately.

[3] A résumé of the data on which the standard ICI luminosity factors are based and of the present status of these factors is given in a paper by Kasson S. Gibson, *Spectral luminosity factors*, J. Opt. Soc. Am. **30**, 51 (1940).
[4] K. S. Gibson, R. P. Teele, and H. J. Keegan, J. Opt. Soc. Am. **28**, 178 (1938).
[5] K. S. Gibson, R. P. Teele, and H. J. Keegan, *An improved luminosity filter*, J. Opt. Soc. Am. **29**, 144 (1939).

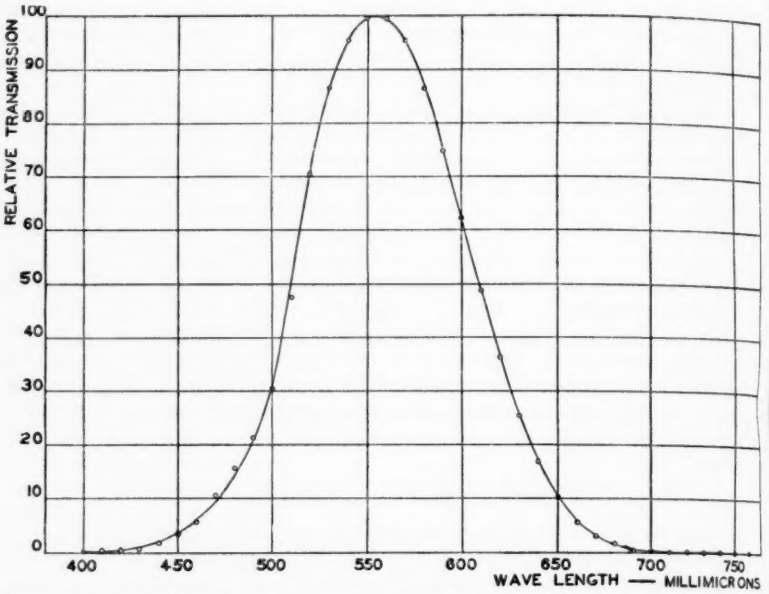

FIGURE 1.—*Relative spectral transmission for the luminosity filter (circles) compared with the standard ICI luminosity curve (continuous line).*

2. RECEIVER

The choice of receiver is dependent upon the reproducibility of its indication, the selectivity, the sensitivity, and the linearity of response with respect to the rate of reception of radiant energy. There are a number of types of receivers whose response to radiant energy is reproducible; hence this requirement does not limit to any considerable extent the choice of receiver. Their selectivity to radiant energy rules out from consideration in the present case receivers such as phototubes and barrier-layer photocells. Although it might be possible to find a combination of a particular selective receiver and filter which together would respond to radiant energy in agreement with the luminosity factors, such a solution to the problem is not yet generally satisfactory because selective receivers even of the same type have differing spectral characteristics. A combination of a filter and a barrier-layer cell which approximates the desired results has been worked out by one manufacturer. This combination is very useful for many purposes which do not require a high accuracy, and refinements in its use have recently been described.[6] In the case of nonselective receivers—such as thermopiles, bolometers, and certain radiometers—the sensitivity and the range over which the response is linear need to be considered together. However, the most sensitive radiometers are either susceptible to various disturbing influences or their range of linearity is too limited. At present there seems to be little choice between bolometers and thermopiles. A thermopile was chosen as the receiver for the present work.

[6] L. E. Barbrow, *A photometric procedure using barrier-layer photocells*, J. Research NBS **25**, 703 (1940) RP1348.

The thermopile used is of the Moll surface type and consists of 80 thermojunctions of constantan-manganin arranged in a circle of 2-cm diameter. The thermopile is designed for use in air and its resistance is approximately 60 ohms.

3. POTENTIOMETER

In preliminary experiments it was found that the voltages were of the order of magnitude of 10 μv (microvolts), and a special potentiometer was accordingly designed to measure such electromotive forces. In work with the completed physical photometer it was found that measurements covering a range from a few tenths of a microvolt to over 100 μv would be necessary in practical photometric work. The potentiometer is capable of covering this range without modification of the original design.

In the measurement of small electromotive forces the most serious difficulty lies in the presence of extraneous thermal electromotive forces in the various parts of the measurement circuit. The major part of the apparatus, comprising the potentiometer, was designed to prevent or eliminate the effects of such electromotive forces.

The galvanometer was selected to work with the combination of thermopile and potentiometer. The potentiometer circuit is such that its resistance is of secondary importance, and a galvanometer was specially built to be critically damped by the thermopile—that is, the critical damping resistance of the galvanometer is approximately equal to the resistance of the thermopile. The galvanometer has, of course, a circuit which is all of copper. The sensitivity is 12 mm/μv for a scale distance of 1 m. The galvanometer is used with a scale distance of 10 m, and the circuit is always reversed to obtain an indication of balance of the potentiometer, which in effect doubles the sensitivity. These two expedients give an effective sensitivity of 240 mm/μv in actual use, and a change of 0.24 mm upon reversal corresponds to 0.001 μv.

4. PRECAUTIONS TO BE OBSERVED

Obviously it is desirable to locate the galvanometer on a vibrationless support. An A-frame support fastened to a heavy masonry wall was found to be adequate for a reasonable percentage of the time.

The thermopile-galvanometer circuit is subject to such disturbances as would be caused by neighboring electric devices, electrostatic and electromagnetic influences, etc. The thermopile should be electrostatically shielded and located as far as possible from all electric equipment. The electrostatic shielding must include the galvanometer circuit. The wires of the thermopile-galvanometer circuit must be fastened down at closely spaced intervals to prevent swinging or movement that would change the magnetic field included by them. Festoons or loops of wire are to be avoided, and the use of twisted pairs of wires is desirable.

III. METHOD OF TAKING OBSERVATIONS

As already stated, the filter transmits radiant energy slightly in the region from 800 to 1,320 mμ in addition to its principal transmission in the visible region. This unwanted energy will also be measured by the receiver. The entire response of the receiver is, therefore,

proportional to the radiant energy transmitted in the visible region plus that transmitted in the infrared. By inserting a filter which does not transmit any visible energy but has a high transmission in the infrared region, the band of energy in the infrared may be evaluated. An infrared (Corning No. 255, sextant red glass) filter will separate the two regions adequately. The measurement must be made in two parts: (1) a measurement of the total energy transmitted by the luminosity filter, and (2) a measurement of the energy transmitted by the luminosity filter and the infrared filter used together.

If we designate the response of the thermopile for the respective measurements outlined above by P_{LT} and P_{LI}, we have

$$P_{LT}=k(E_{LV}+E_{LI}) \tag{1}$$

and

$$P_{LI}=kE_{LI}F_I, \tag{2}$$

in which k is a proportionality constant, E_{LV} is the energy from the source transmitted by the luminosity filter in the visible region only, E_{LI} is the energy from the source transmitted by the luminosity filter in the infrared region only, and F_I is the infrared transmission factor for the infrared filter. From eq 1 and 2 it is seen that the response, P_{LV}, in the visible region alone is

$$P_{LV}=kE_{LV}=P_{LT}-kE_{LI}=P_{LT}-\frac{P_{LI}}{F_I}. \tag{3}$$

As a preliminary to the use of the physical photometer, it is therefore necessary to determine the infrared transmission, F_I of eq 2 and 3, of the infrared filter to be used. This may be done by using the physical photometer to measure the transmission of the infrared filter for energy from an incandescent source passing through a similar infrared filter. This determination has been carried out for incandescent sources over the color-temperature range 2,046° to 2,842° K, and F_I was found to be constant at 0.70 within ± 0.01. For such sources this uncertainty in F_I introduces at most an error of 0.2 percent of the luminous flux. Therefore the determination of F_I for the usual incandescent source can be made at an intermediate color temperature once for all.

The total response of the thermopile-galvanometer circuit is caused both by the radiant flux from the source being measured and by stray or extraneous flux from the surroundings. By the surroundings are meant the laboratory room and its contents, including the persons who are operating the equipment.

The electromotive force caused by the radiant flux from the source is distinguished from the rest by the use of a shutter to allow the flux being measured to reach the receiver at desired times. The shutter used should be designed and placed so that its operation will not change the conditions of the surroundings or cause air currents around the thermopile. In the present work a rotary shutter made from a disk of plywood with an opening to let the energy pass through to the receiver proved to be satisfactory. By placing this shutter between the source and the luminosity filter, the latter can be used as a window for the thermopile housing and thus reduce materially the trouble from air currents which would be encountered in using an uncovered thermopile.

The surroundings are, in general, not at the same temperature as the thermopile, and thus there is an exchange of radiant energy between the thermopile and the surroundings. The thermoelectromotive force of each of the junctions is about 40 μv/°C, and hence the total for the 80 junctions is more than 3,000 μv/°C. Since it is sometimes desired to make measurements imprecise by less than 0.001 μv, the receiver surface and the dark junction cannot be considered to be at the same temperature unless their temperatures differ by less than about 3×10^{-7} of a degree centigrade. It is not practical to maintain these temperatures within such small limits, and it is, therefore, neces-

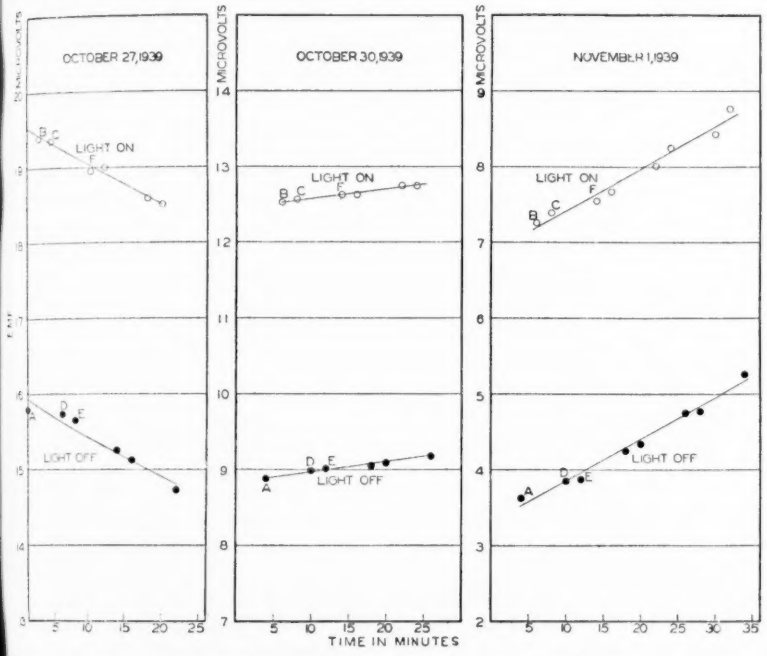

FIGURE 2.—*Response for a 300-watt lamp at a distance of 1.56 meters at constant voltage.*

Observations were taken at 2-minute intervals.

sary to eliminate the effect of the stray energy by an accurate timing of the measurements of the response when the receiver is screened from and when it is open to the energy from the source. Gradual warming or cooling of the surroundings causes a first-order drift in response due to stray energy, and second-order changes are avoided by taking precautions to prevent sudden changes in conditions of the surroundings—that is by keeping doors and windows closed, by having the operators located at a distance from the thermopile housing, and by keeping equipment located in one position during a series of measurements.

Figure 2 shows readings taken with a 300-watt lamp at a distance of 1.56 meters on different occasions. These readings are taken in the following manner. The light source is turned on and the potenti-

ometer approximately balanced with the shutter closed. Temperature equilibrium is reached in the course of 2 or 3 minutes. An accurate balance is then obtained and the shutter opened. After a definite time interval, say 2 minutes, another reading is taken. The shutter is kept open for the chosen time interval and another reading taken and the shutter closed. After 2 minutes a reading is taken. The shutter is kept closed for an additional 2 minutes and a reading taken. This cycle is continued for a group of three or four pairs of readings. The time interval will depend to some extent upon the ability of the potentiometer operator, but it should be as short as is consistent with the determination of accurate balances of the thermopile-galvanometer circuit and of the potentiometer. The time necessary for the thermopile to reach thermal equilibrium determines the shortest permissible interval. For the thermopile used, this time is approximately 10 seconds. A time interval of 1 or 2 minutes was found to be satisfactory.

Figure 2 is for illustrative purposes only, and in actual use a definite time interval is used and the average of two adjacent light-off readings is subtracted from the average of the corresponding adjacent pair of light-on readings to obtain the response to the energy being measured; for example, the average of points A and D subtracted from the average of points B and C. Obviously, the average of points D and E subtracted from the average of points C and F also represents the response to the energy being measured. The 3 days shown in the figure include a day on which the initial light-off reading was comparatively large and the drift was negative, a day when the drift was small, and a day when the drift was strongly positive.

The data shown in figure 2 indicate that results of fair precision may be obtained from a light-off, light-on, and light-off reading at approximately equal time intervals. It is also obvious that when the response is large, say 50 to 100 μv, the necessity for accurate timing is greatly reduced. For example, in the section of figure 2 for November 1, 1939, the entire time is over half an hour; and it is apparent that if a light-off reading were taken at point A, and a light-on and light-off reading were taken at any time during the next half hour, an error of less than 1 μv would be caused by neglecting time altogether and considering the average of the two light-off readings as representing the light-off conditions. If the vertical separation were 100 μv, as it may often be, this 1 μv would represent an error of only 1 percent. Usually, readings may be taken in a time interval of a few minutes rather than half an hour. If an uncertainty of 1 or 2 percent can be tolerated, it is possible to simplify the procedure and use more rugged, but less sensitive, electric equipment.

IV. EXPERIMENTAL TESTS

The physical photometer was tested experimentally by measuring spectrally selective filters to verify the adequacy of the luminosity filter and thermopile and by measuring rotating sector disks to be sure that the rotating lamps would be evaluated correctly.

1. MEASUREMENT OF SPECTRALLY SELECTIVE FILTERS

The glasses measured were chosen from types that are very selective in their transmission and were selected so as to include transmission bands distributed throughout the visible spectrum. The group included those designated as selenium red, selenium yellow, signal yellow, cobalt blue, signal green, and signal blue, the glasses ranging from 2 to 50 percent in transmission, and also signal-purple filters some of which transmitted only one-half of 1 percent of the incident light from an incandescent lamp at 2,848° K. Their spectral transmissions and the computed luminous transmissions had been carefully determined by others, and the data for many of them have been published.[7]

In the measurement of the luminous transmission factor, F_V, of a glass filter, four measurements have to be taken, corresponding to eq 3, with the glass in the beam and with it removed. The value of F_V is given by the ratio

$$F_V = \frac{\left(P_{LT} - \frac{P_{LI}}{F_I}\right)_{\text{glass in}}}{\left(P_{LT} - \frac{P_{LI}}{F_I}\right)_{\text{glass out}}}. \tag{4}$$

The comparison of the results of measurements made with the physical photometer according to eq 4 and the values obtained by computation from spectrophotometric data by the use of the ICI luminosity factors is given in table 1. The values calculated from spectrophotometric data were computed by the usual summation method with 10-mμ intervals, although this computation by discrete intervals may slightly reduce the accuracy of the final result. The response of the physical photometer is equivalent to a continuous intergration rather than to the summation used in the computations. On the other hand, the physical photometer data were obtained at room temperatures, whereas the spectrophotometric data, on which the computations are based, were obtained at 25° C. It so happens that the selenium red and yellow glasses, which are subject to appreciable summation errors, are also the least uniform in transmission (through different parts of a given filter) and subject to the largest temperature effects.[8] The discrepancies between the two columns of values are well within the combined experimental errors of the two methods for all of the glasses.

The test with these 22 filters justifies the conclusion that the physical photometer gives results which are consistent with the ICI luminosity factors and verifies the performance of the combination of luminosity filter and thermopile-galvanometer-potentionometer system.

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[7] K. S. Gibson and Geraldine K. Walker, Signal Section, Proc. Am. Ry. Assn. **30,** 405, 420 (1933).

[8] The purple glasses are also subject to appreciable summation errors and important temperature effects but are uniform in transmission.

TABLE 1.—*Comparison of values of luminous transmission of spectrally selective glasses obtained by direct measurement with the physical photometer and by computation from spectrophotometric data with ICI luminosity factors*

Color designation of glass	Luminous transmission for 2,848° K		Color designation of glass	Luminous transmission for 2,848° K	
	Physical photometer	Spectrophotometer		Physical photometer	Spectrophotometer
Selenium red	0.088	0.089	Signal green	0.182	0.184
Do	.103	.101	Do	.200	.201
Do	.135	.139	Do	.251	.252
Selenium yellow	.505	.500	Do	.268	.270
Signal yellow	.378	.376	Signal blue	.0356	.0356
Do	.506	.508	Do	.0215	.0216
Cobalt blue	.163	.161	Signal purple	.0049	.0051
Do	.244	.242	Do	.0050	.0049
Do	.291	.290	Do	.0063	.0059
Do	.374	.374	Do	.0115	.0120
Do	.402	.400	Do	.0200	.0206

2. MEASUREMENT OF ROTATING SECTORED DISKS

When sectored disks are used, the light reaching the receiver varies from zero, when the opaque portion is in the path of the light, to full intensity, when the open portion is in the path of the light. Obviously, the use of sectored disks is a more severe test of the physical photometer than the evaluation of a rotating lamp for which the changes in intensity are small.

The transmissions of two sectored disks, one with four openings, transmitting about 10 percent, and one with two openings, transmitting about 1 percent, were measured on the physical photometer. The transmissions of the sectored disks were also calculated from the angular openings.[9] The calculated and measured transmissions are compared in table 2.

The results given in table 2 indicate that the physical photometer will correctly evaluate an intermittent light when the periods of fluctuation are short compared with the response period of the thermopile-galvanometer circuit (about 10 seconds). Any period can be used provided it is not great enough to cause perceptible flicker of the galvanometer spot.

TABLE 2.—*Comparison of transmissions of sectored disks*

Disk designation	Transmission factor	
	Calculated from angular opening	Measured by the physical photometer
10 percent	0.1000	0.1001
1 percent	.00979	.00975

[9] The angular openings were determined by the Length Section of the Weights and Measures Division of the Bureau.

3. STABILITY

One important consideration is the stability of the physical photometer. In measuring lights it is desirable to have an instrument which can be calibrated and then used for a period of time before recalibration. The length of time between calibrations is governed by the possible aging effects of the component parts of the physical photometer.

The surface of the receiver is well protected from mechanical damage, and there is no reason to expect that rapid changes will occur from aging of the surface. The chemicals used in the luminosity filter are all stable in the concentrations used in the solution. Most of the constituents have been carefully studied by other investigators.[10] The properties of the glass are not likely to change.

Nevertheless, the stability was investigated by two separate tests. A seasoned lamp was placed at a fixed distance from the receiver and measured over a period of 2 weeks. The results are given in table 3. A study of these data shows a maximum variation from the mean of 0.35 percent and an average deviation of 0.17 percent. These variations are within the experimental error, and this test shows that during this length of time there was no appreciable change in the emf of the thermopile for a given density of luminous flux.

TABLE 3.—*First test of stability*

Date	Response
	Percent
March 23	100.17
March 25	99.92
March 28	100.30
March 31	100.04
April 1	99.65
April 6	99.92
Mean	100.00

The second test was made as part of a series of measurements on a group of standardized lamps. The period of time covered by this series of measurements was nearly 6 months. The response for a given density of luminous flux during this period did not vary by as much as 0.4 percent from the mean, and the average deviation from the mean was less than 0.2 percent.

V. APPLICATION TO MEASUREMENT OF LAMPS

The results obtained in measuring highly selective filters, given in table 1, indicate clearly that the physical photometer may be used to measure the light from all spectral types of sources, including fluorescent lamps, mercury, neon, sodium, and similar gaseous-discharge lamps. Parker [11] has already used a similar physical photometer for work with mercury and sodium lamps.

[10] R. Davis and K. S. Gibson, Filters for the Reproduction of Sunlight and Daylight and the Determination of Color Temperature, Misc. Pub. BS 114 (1931).

[11] Allan E. Parker, *Measurement of illumination from gaseous discharge lamps*, Illum. Eng. 35, 883 (1940).

The values obtained for the rotating sectored disks (table 2) show that fluctuating sources, such as rotating lamps and gaseous-discharge lamps (operating on alternating-current circuits), will be correctly integrated when the period of the fluctuation is not long compared with the response period of the thermopile-galvanometer circuit.

The work done with the physical photometer indicates that, when once calibrated, it will enable the candlepower of a lamp to be determined without the use of other lamps as standards and without the use of accessories, such as color-matching filters. Visual observers must balance a lamp against other lamps of known candlepower in order to determine the candlepower of the unknown lamp; little time can intervene between the photometric balances for the different lamps; and when the lamps being compared differ in color, it is necessary to use accessory filters to equalize the color. The use of a previously calibrated physical photometer to determine the candlepower of a lamp will be of considerable advantage in conserving the life of standard lamps and will result in a saving in the time required to determine the candlepower of a single lamp. In addition, it will be unnecessary to take time to obtain and to calibrate a color-matching filter, when such a filter is required as an accessory for visual observations.

Another advantage of the physical photometer is that one person, experienced in using sensitive electric-measuring equipment, can make the measurements required and thereby save most of the time and trouble involved in obtaining and using a group of visual observers who have photometric experience and nearly normal luminosity functions.

Work leading to the use of the physical photometer for the determination of the candlepower of lamps operating at 2,046°, 2,360°, and 2,727°K to give three points on the new proposed photometric scale [12] is under way.

VI. SUMMARY

The experimental results show that a physical photometer composed of three elements—a luminosity filter, a spectrally nonselective receiver, and a sensitive electric measuring apparatus attached to the receiver—gives photometric results which are practically the same as those which should be obtained by a standard observer having the characteristics represented by the ICI luminosity factors.

The luminous transmission of a spectrally selective filter can be determined with the physical photometer in a much shorter space of time than that required to obtain the spectrophotometric data and perform the necessary calculations. The two methods are comparable in accuracy. It is often unfeasible to make such determinations by direct visual observation.

WASHINGTON, July 1, 1941.

[12] E. C. Crittenden, *Terminology and standards of illumination*, J. Opt. Soc. Am. **29**, 103 (1939).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1416

Part of Journal of Research of the National Bureau of Standards, Volume 27, September 1941

COMPARISON BETWEEN THE OBSERVED DENSITY OF CRYSTALLINE RUBBER AND THE DENSITY CALCULATED FROM X-RAY DATA

By W. Harold Smith and Nancy P. Hanna

ABSTRACT

The density of crystallized rubber may be determined directly or may be computed from the dimensions of the unit cell, which is deduced from X-ray patterns. In early computations, the density obtained was greater than unity, but in recent work computed values have decreased, the lowest quantity reported in the literature being 0.965. In the work described here, there have been determined by direct experiment, the densities of amorphous rubber, of unstretched crystallized rubber, and of rubber crystallized as completely as possible by stretching it. At 25° C, the density of amorphous smoked sheet was found to be 0.906. With purified, amorphous petroleum ether-sol rubber, the values ranged from 0.899 to 0.902 with different preparations of material. At −10° C, the density of crystalline, unstretched smoked sheet varied from 0.950 to 0.952; that of crystalline petroleum ether-sol rubber ranged from 0.948 to 0.951. The density of amorphous smoked sheet at −10° C was 0.932, which was calculated from the value of 0.906 observed at 25° C. That of amorphous petroleum ether-sol at −10° C was 0.928, based on 0.902 observed at 25° C. Smoked sheet stretched almost to the breaking point, and crystallized further at −15° C, had a density of 0.960 at −10° C. Stretching caused an increase, not more than 0.01 greater than that of unstretched crystallized rubber. The increase in stretched rubber is generally believed to be caused by a form of packing in crystallization of a fibrous type. It is reported in the literature that the density becomes constant at 2,000-percent elongation when rubber is racked. Its value, observed presumably at a room temperature, was 0.953. The density at 2,000-percent elongation appears to be that of completely crystallized rubber, and when corrected for the temperature used in any X-ray investigation, is a reasonable guide for deductions about structure.

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I. INTRODUCTION

When unvulcanized rubber is stretched quickly, an orientation of structure occurs parallel to the direction of extension, which is usually regarded as a form of crystallization because of the optical and other phenomena which accompany it. It is also accompanied by a change of volume. When unstretched rubber is subjected to suitable temperatures below about 10° C, it too becomes crystalline. The crystallization of rubber is accompanied by an increase of density, and the simultaneous production of an X-ray diffraction pattern is usually interpreted as evidence that crystallization has occurred. A diffraction pattern of this kind results from the regular repetition, within the crystal structure, of groups of atoms or molecules in a definite spatial arrangement. The smallest group from which the structure can be built up in this way is called the unit cell; and the dimensions can be computed from measurements of the pattern, provided it is possible to determine the crystal form. The pattern of stretched rubber consists of interference spots, and that of frozen rubber consists of rings, but both of their measurements have been shown to indicate the same unit cell. If, in addition, the number of atoms in the unit cell is known, the density of the material can be computed. If the computed density agrees with that found by direct measurement, the fact is a valuable indication of the correctness of the assumed structure on which the calculation of density was based. Accurate knowledge of the density of completely crystallized rubber would therefore serve both as a guide in studies of structure and as a measure of the degree of crystallization of any material under consideration.

In the experimental work described in this paper the rubber was crystallized as completely as possible. Its density was determined by recognized methods and compared with the densities calculated from X-ray measurements.

II. REVIEW OF PREVIOUS WORK

The densities obtained by calculation from X-ray investigations have recently been summarized by Gehman [1].[1] The values vary with the assumptions regarding the unit cell. Until lately they were greater than unity but have tended to decrease in the course of more recent work. The lowest value found in the literature now is 0.965 [2]. The densities measured directly have been less than the computed values, and the differences have been difficult to explain. Perhaps further interpretations of X-ray patterns will reconcile them.

The rhombic cell postulated by Mark and von Susich [3], which undoubtedly had an influence on the configurations assumed in later hypotheses, required that crystallized rubber should have a density of 1.08. According to later measurements of Lotmar and Meyer [4], who assumed that the cell is monoclinic, it should be 1.02. Sauter [5] described another rhombic cell based on the assumed existence of a double reflection. The density computed from this cell is 0.974. Morss [2] attempted to find the true unit cell of rubber, but his conclusions were not entirely satisfactory. The basis of his deductions is a change from 90° to 109.5° of the angle between the two inde-

[1] Figures in brackets indicate the literature references at the end of this paper.

pendent sets of planes which reflect the two strong equatorial spots. With this modification, the calculated density of the unit cell is 1.00. When Morss applied the angle 109.5° to the measurements of Lotmar and Meyer, the value was 0.965. Misch and van der Wyk [6] have recently obtained photographic evidence of the double reflection which was assumed to exist by Sauter. The cell they postulated resembles that of Morss but contains 16 isoprene units; the calculated density is 0.970.

In the publications of Lotmar and Meyer and of other investigators mentioned above, it is evident that the density 0.965 was accepted as the value to which the unit cell of rubber should conform. This same value was observed by direct measurement by Kirchhof [7], who used smoked sheet which had been stretched to 900-percent elongation and then subjected to a fitting low temperature for further possible crystallization. In the unstretched amorphous state, the density of his material was 0.942. As this value is considerably higher than any of those listed by Wood [8], and as no temperature is mentioned, the determination was probably made at temperatures lower than 25° C or the smoked sheet may have contained abnormally heavy impurities. Lotmar and Meyer, however, obtained the same experimental value as Kirchhof with a crystalline material which was prepared by the evaporation of a solution of rubber in benzene, and subsequently crystallized, but they also did not mention the temperature of measurement. The rubber was held in a well-stretched state at 0° C for 24 hours before the determination.

III. EXPERIMENTAL WORK

1. PREPARATION OF MATERIAL

Because the impurities are disregarded in calculating the density of rubber from X-ray measurements, it was believed desirable to purify rubber for direct determinations. Feuchter [9] has shown that sol fractions of raw rubber are almost free from nitrogen and otherwise quite pure. Accordingly, in the work to be described, unstretched and stretched petroleum ether-sol fractions were used. Smoked sheet and dried latex were also examined for comparison. The rubber used to prepare the petroleum ether-sol had received the following treatment. The latex of *Hevea Brasiliensis*, protected from contamination by bacteria with sodium ethylmercurithiosalicylate, was digested with trypsin to degrade the protein which is in the latex. The water-soluble products of this treatment were largely removed by creaming the rubber three times with a 0.2-percent solution of sodium alginate and withdrawing the layer beneath the creamed material. A small amount of natural antioxidants, equivalent at least to that in raw rubber [10], was added to the rubber dispersion after each separation. After the third separation, the upper layer was centrifuged to remove dirt and was then diluted with distilled water until it contained about 1 percent of rubber. By freezing the diluted dispersion, a loose porous coagulum was formed; and after the ice had melted, residual water-soluble impurities were removed by washing the coagulum with successive portions of distilled water. From the dried product a petroleum ether solution of sol was prepared by a procedure similar to that used earlier. After the sol fraction was separated from the gel,

the petroleum ether was removed by evaporation. Films formed by the evaporation of solutions of rubber in benzene at room temperature were usually free from air bubbles. The residue of sol rubber was dissolved in benzene of reagent quality, and the solution was transferred to an evaporating dish. Transparent, colorless films were formed about 2 mm thick. Rubber which had deposited on the sides of the dish was cut away. The dish was placed in distilled water, and when the deposit on the bottom could readily be detached, samples weighing between 1 and 1.5 g were cut to a suitable shape under water. The samples were dried to constant weight at 100° C in a stream of nitrogen.

With the purpose of increasing mobility during crystallization at a suitable low temperature, a plastic rubber was prepared by disaggregating with piperidine a sol fraction dissolved in benzene. The piperidine was subsequently extracted from the product with successive portions of acetone, at room temperature. After the disaggregated rubber had been chilled at −10° C for 30 minutes, it could be elongated to at least twice its original length.

2. METHODS OF CRYSTALLIZATION

The marked discrepancy between the calculated and experimentally determined values persisted in spite of the precise X-ray measurements of Lotmar and Meyer, and may well cast doubt on the experimental value if the assumptions leading to the calculation of the axes of the unit cell are accepted. Consequently it seemed possible that by some special experimental procedures rubber could be crystallized to a higher degree and thus have a higher determined density than any reported in the literature. Some of the procedures were based in part on the conception of the rubber molecule as a long chain with angular configuration. The chains, if they are assumed to exist as a tangled, interlacing mass and to possess secondary valence forces, can perhaps be oriented with difficulty. It was thought that very slow elongation might cause more perfect alinement because, under this condition, the forces of attraction and repulsion along the sides of the molecule would be given greater freedom. Strips about 25 mm wide and 1 mm thick were stretched at various slow rates, at room temperature and also at −10° C and at −20° C, immediately after they had become chilled. To determine the effect of rapid stretching, other strips were extended suddenly at these temperatures. According to another concept of rubber structure, needle-shaped molecules may exist in groups of micelles. During disaggregation, a separation of the molecules might be expected to occur, accompanied by increased mobility. Strips of disaggregated rubber were chilled to −10° C and to −20° C to decrease mobility and minimize any disorganization caused by the heat of stretching, and then stretched quickly to maximum elongation. Others were stretched in successive small steps to maximum elongation during 20 minutes, before crystallization became pronounced. None of the various special methods described above had any effect. The samples with which the results in table 1 were obtained had been subjected to temperatures of about −15° C for different periods, none longer than 30 days, before the determinations were made.

3. METHODS OF DETERMINING DENSITY

The densities were determined by the hydrostatic method in an immersion mixture consisting of equal parts by weight of acetone and water. They were also determined by adjusting the amounts of acetone and water until the mixture had the same density as the specimen, and the density of the mixture was determined. The hydrostatic method involved the use of an analytical balance. A strip of rubber about 70 mm long, which had been cut with chilled shears, was held on a stiff platinum wire, the end of which was bent to form a rigid support. The immersion mixture was contained in a Dewar flask, and its density was found with a precision type of Westphal balance, suitably corrected. The determinations were made usually to about one-thousandth of a unit. If greater precision was desired, the effect of the cold immersion mixture on the arm of the balance was noted, a small amount of a suitable wetting agent was added to minimize surface drag on the wire, and the observations were made as rapidly as possible. Since some forms of crystalline rubber have sometimes been observed to melt below 0° C, a temperature of −10° C was used in this work for density determinations of crystalline material, to avoid melting and also to suppress the tendency of the rubber to swell in the acetone-water mixture. With amorphous rubber, a temperature of 25° C was used, and the sample was attached to a sinker in distilled water as the immersion liquid. Air which adhered to the surface of a specimen immersed in water, or in a mixture of water and acetone, was removed. After a determination of density, the sample was dried in air and placed in dimethyl phthalate, which has approximately the refractive index of rubber. Air in the sample was readily observed, and when necessary the amount of it was estimated.[2] The highest correction applied to the density because of included air was 0.001.

IV. RESULTS FROM DENSITY DETERMINATIONS

Typical values of the density of amorphous rubber and of crystalline rubber at −10° are given in table 1. With crystalline unstretched smoked sheet, the results vary between 0.950 and 0.952; and with crystalline unstretched petroleum ether-sol, they range from 0.948 to 0.951. The results which show the effect of stretching upon smoked sheet represent successive elongations of 100 percent. The increase in density is slight, not more than 0.01. The last quantity, 0.960, was obtained with a sample extended beyond 1,000 percent, almost to the breaking point. Higher densities than 0.960 were possible only by racking the rubber. The density of amorphous smoked sheet at −10° C is calculated by the formula of Bekkedahl [11], using the value 0.906, which was observed at 25° C; that of amorphous sol rubber from 0.902, the highest density observed with this material at 25° C. This value is lower than any of the values listed by Wood [8]. However, in addition to this quantity of 0.902, other densities were observed ranging as low as 0.899 with different lots of sol rubber. Repeated observations with any single preparation agreed to the third decimal place. In spite of attempts to find a source of error, the differences in different lots of sol rubber persisted.

[2] By C. P. Saylor, of this Bureau.

TABLE 1.—*Densities of amorphous rubber and of crystalline rubber at −10° C*

[The densities of amorphous rubber at −10° C were calculated from values obtained at 25° C]

Petroleum ether-sol		Smoked sheet			
Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Amorphous unstretched (−10° C)	Crystalline unstretched (−10° C)	Crystalline stretched (−10° C)	
				Density	Elongation
					%
0.928	0.946	0.932	0.951	0.954	100
	.945		.952	.956	200
	.944		.951	.956	300
	.943		.950	.956	400
				.956	500
				.957	600
				.957	700
				.957	800
				.958	900
				.958	1,000
				.960	>1,000

In addition to the values listed, some determinations were made with miscellaneous samples prepared in various ways. When dried strips, prepared by the evaporation of dialyzed latex, were extended to various amounts between 100-percent and 1,000-percent elongations and subjected to a temperature of −15° C while stretched, their densities were the same as those observed when smoked sheet was elongated (table 1), and stretching caused an increase of not more than 0.01. The density at −10° C of disaggregated rubber after chilling was 0.951, which is in the range observed with sol rubber. That of smoked sheet which had been stored without pressure at 0° C for approximately 5 years was 0.957 at −10° C. To determine the effect of pressure in the absence of orientation, sol rubber was placed in a square, confined space with sides about 1 cm², and squeezed by a piston under a pressure of about 1,000 atmospheres, at room temperature for 8 hours. While the pressure was maintained, the rubber was crystallized during 12 hours, at −10° C. Its density was 0.951. The same value obtained without pressure is listed in the table of results. Pressure from all sides of the confining space did not in this case increase the density.

The rate at which rubber crystallizes at −20° C was observed with unstretched specimens cut from adjacent areas of a smoked sheet. The initial density, 0.929, of amorphous rubber at −20° C was calculated from Wood's publication [8] on physical constants of rubber, because crystallization occurred during attempts to determine it. The densities at successive intervals were as follows: after 3 hours, 0.935; 5 hours, 0.950; 24 hours, 0.955; 1 week, 0.955. When these values were plotted, a curve was obtained which was similar in shape to that reported by Bekkedahl [11] for the rate observed at 0° C. At −20° C the transition was faster.

In earlier work [12] stretched rubber, maintained in an extended state, was observed to increase in length when subjected to suitable low temperatures. According to the explanation which was suggested, stretching establishes a crystal lattice with crystals oriented parallel to the direction of elongation, and when more molecules enter it,

they too assume the parallel direction. The rubber elongates because of the shape of the molecule until molecular movement is inhibited by random crystallization of the residual rubber. To determine whether a marked change of density occurs during the secondary extension, the following procedure was used. A strip of uniform width and thickness from dried latex was extended, fastened at both ends and at the middle, forming two sections, and immediately exposed to a temperature of −20° C. When the extension had definitely commenced, a specimen was cut from one section and its density determined as quickly as possible by the hydrostatic method to a ten-thousandth of a unit. After the extension had become completely established, about 20 minutes later, a specimen from the second section was examined. The amount of elongation was the difference between the length of the specimen after its density had been determined, and the length after the specimen had subsequently been allowed to retract at room temperature for 24 hours. With one sample the density before secondary extension was 0.9449 and the elongation 380 percent; at maximum secondary extension it was 0.9456 at an elongation of 440 percent. With another sample the density before secondary extension was 0.9386 at 130-percent elongation, and 0.9391 afterward at 195-percent elongation. The increase of density with the first sample, 0.0007, during a secondary extension of 60 percent, amounts to 0.0071, when the increase is based on 1,000-percent elongation less the original elongation before secondary extension took place. The increase of density of the second sample, 0.0005, during a secondary extension of 65 percent, becomes 0.0067 on the same basis. These increases agree closely with the results obtained with smoked sheet, based on 1,000-percent elongation, in table 1. There the minimum increase is 0.006 and the maximum 0.008.

V. DISCUSSION OF RESULTS

The change of volume which takes place during the elongation of rubber appears to be the result of the formation of crystals of the same type as those formed when rubber is cooled. The fact that calculations of the dimensions of unit cells from X-ray data lead to the same result in the two cases suggests this. The increase of density during elongation is usually ascribed to a form of packing in crystallization of an oriented fibrous type, which takes place. The increase continues during racking, but becomes constant at 2,000-percent elongation, at which Feuchter [13] found a density of 0.953, apparently at some room temperature. If a probable temperature of 20° C is assumed, at −10° C it would be 0.970.

If density is to be used to aid in the interpretation of X-ray diffraction patterns, the effect of temperature should not be disregarded, because rubber has a large coefficient of expansion.

The density of rubber, completely crystallized when stretched, appears to be the limiting density reported by Feuchter, for the following reason. In X-ray diagrams of stretched rubber, the position of the diffraction spots is independent of the elongation but the spots become more intense as the elongation increases, that is, with the increase of packing. This suggests that the maximum effect represents an orientation that is substantially complete. Recently, Field [14] developed a method of measuring the amount of crystallinity in stretched rubber. At high elongations the maximum amount found was about 80 percent of the total. For total crystallinity a density

of 0.965 was deduced. Treloar [15] estimates that the increase of density during crystallization is not less than 3.75 percent. The reports of several observers, who have examined types of sol and gel rubber of varying degrees of aggregation by X-ray technique, indicate that crystallinity is developed and retained most readily in the stretched gel fraction. Consequently, when rubber is stretched there appears to be a relation between the degree of polymerization and the amount of crystalline material formed.

The range of densities, 0.899 to 0.902, observed with amorphous petroleum ether-sol rubber in this work is much less than the differences shown by results reported in the literature and summarized by Wood [8]. The following values are quoted from the summary. With unpurified rubber at 25° C, Bunschoten found a density of 0.905; Whitby, 0.906; McCallum and Whitby, 0.918; and Feuchter, 0.928. With purified rubber at the same temperature, Weber found 0.905; McPherson, 0.906; McCallum and Whitby, 0.9207; and Bondy (Staudinger), 0.9208. Recently Kemp [16] reported densities of petroleum ether-sol rubber, determined at 20° C, which varied from 0.905 to 0.910. At 25° C, this corresponds to a density range from 0.902 to 0.905. With impure and with purified material, the lack of agreement is significant, and the densities of sol rubber, 0.899 to 0.902, agree with none of the values quoted. Perhaps the low values obtained in this work represent the densities of depolymerized material. By this term is meant a disruption of long-chain molecules into short ones characterized by lowered viscosity and molecular weight, and decreased tensile strength. In long-chain molecules of high molecular weight, for example 100,000, forces of attraction and repulsion at the ends must be negligible. The molecule substantially is one consisting of two sides. If the long molecule is broken into many short ones, it is possible that disruption may continue until the ends of short molecules cause significant attraction and repulsion. An increase of volume would result. Unfortunately, nothing is known about the degree of depolymerization which is necessary to cause a change of volume. Furthermore, any proposed explanation for the ranges of density observed must be viewed with skepticism, because no structure which has been proposed for rubber has received complete acceptance.

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ERRORS OF MUNSON AND WALKER'S REDUCING-SUGAR TABLES AND THE PRECISION OF THEIR METHOD

By Richard F. Jackson and Emma J. McDonald

ABSTRACT

In a recent investigation (RP1301) Hammond has undertaken a comprehensive revision of the Munson and Walker reducing-sugar tables and has disclosed discrepancies much greater than the experimental errors of analysis. It is now shown that the main cause of these discrepancies was the contamination of the cuprous oxide, which Munson and Walker weighed directly for the estimation of copper. An independent series of analyses made by the authors, who determined copper iodometrically, was found to be in good agreement with the analyses of Hammond, who determined the copper electrolytically. The recommendation is made that Hammond's copper equivalents be adopted in substitution of those of Munson and Walker.

A series of determinations by Erb and Zerban of invert sugar in the presence of sucrose in aliquots containing 0.4 g of total sugars in 50 ml of solution are in agreement with those of Hammond at high concentrations of invert sugar, but deviate at lower concentrations. The present series of analyses are in agreement with those of Hammond at these discrepant points.

Detailed methods of copper analyses are described. A new modification of the dichromate method is given in which the end point is determined both colorimetrically and electrometrically.

Methods for the preparation of standard invert sugar by hydrolysis of sucrose are discussed.

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I. INTRODUCTION

In recent years, advances in reducing-sugar analysis have consisted mainly in improvements in volumetric processes, especially those which permit the entire analysis to be completed in a single reaction vessel. While these methods are of most general service, the older methods which require filtration of cuprous oxide still serve a useful purpose, particularly when but an occasional analysis is required or the sample is seriously contaminated or discolored. The gravimetric methods have the disadvantage of being more time-consuming than the volumetric processes, but when modified by the introduction of volumetric methods for the determination of reduced copper, they approach the volumetric methods with respect to convenience and rapidity.

Practically the only one of the older gravimetric methods which has survived in this country and which indeed is still extensively employed at the present time is the method of Munson and Walker [1].[1] This method has the advantages of extreme simplicity and, as will be shown, high precision. Munson and Walker, in establishing their fundamental tables in 1906, analyzed the respective pure sugars, determining the reduced copper by weighing as cuprous oxide, which they then converted to copper by the stoichiometrical factor. Erb and Zerban [2] redetermined the copper values for sucrose-invert sugar mixtures containing 0.4 g of total sugar. Their results were in agreement with those of Munson and Walker for the middle range of concentrations, but in disagreement at the higher concentrations.

Recently Hammond [3] has made a comprehensive revision of the tables for dextrose, levulose, invert sugar, and three series of mixtures of sucrose and invert sugar containing, respectively, 0.3, 0.4, and 2.0 g of total sugar. Many of the copper values found by Hammond differ from those of Munson and Walker by amounts far greater than any probable experimental error. In view of the importance of these tables, it seemed advisable that a third series of analyses be made in order that one or the other set of values might be corroborated. It was the purpose of the present investigation to contribute a third series and to determine, if possible, the source of the discrepancies between Hammond's and Munson and Walker's copper equivalents.

II. METHODS OF ANALYSIS

1. MATERIALS AND REAGENTS

(a) SOXHLET REAGENT

The Soxhlet reagent was prepared in the usual manner by mixing 25 ml of each of the two constituent solutions immediately before the analysis. The copper solution contained 34.639 g of copper sulfate crystals in 500 ml of solution. The solution was allowed to stand for several days and was then filtered through fritted glass. The crystals were usually deficient in copper by 1 to 2 percent, and thus the copper content of the filtrate required adjustment to 440.9 mg in 25 ml. For the median range of sugar concentrations it is apparently unimportant that the copper be adjusted accurately to the specified value; but at the higher concentrations when the copper

[1] Figures in brackets indicate the literature references at the end of this paper.

approaches exhaustion, it is important that the copper content conform to the specification.

The alkaline tartrate solution contained 173 g of Rochelle salt and 50.0 g of sodium hydroxide in 500 ml of solution. The sodium hydroxide was freed from carbonate by allowing a 50-percent solution to stand overnight and filtering through asbestos or fritted glass. The alkali content of the filtrate was determined by titration of weighed samples.

(b) SUGARS

Dextrose and levulose.—The dextrose (Standard Sample No. 41 of this Bureau), which had been prepared by crystallization from aqueous solution in the anhydrous crystalline form, showed no loss in weight upon heating at 110° C for 2 hours. The levulose, which had been prepared by crystallization from aqueous solution, was further purified by twice recrystallizing from aqueous alcohol [4]. During the first recrystallization a volume of nitric acid stoichiometrically equivalent to the inorganic impurities was added. The final crystals, dried at 70° C, showed an ash content of less than 0.002 percent and an absence of moisture when dried in a thin layer for 2 hours at 70° C.

Invert sugar.—For most of the analyses invert sugar was prepared by taking equal weights of pure dextrose and levulose. Hammond prepared his invert sugar in the same way; but his data, in spite of the high purity of the substance, showed considerably lower yields of copper than those of Munson and Walker, who prepared invert sugar by hydrolysis of sucrose with 0.02 *N* hydrochloric acid for "one-half hour on the water bath." It was thought at first that the differences in the observed reducing power might be due to differences in the invert sugar. An effort was accordingly made to reproduce Munson and Walker's measurements.

The velocity of inversion of cane sugar is in the highest degree a function of the temperature. Hence merely placing a solution on the water bath without regarding the temperature actually attained leads to uncertain results. In one instance such an experiment produced a preparation which was but 83 percent inverted. Jackson and Gillis [5] derived formulas which enabled us to calculate the velocity of inversion as a function of temperature and concentration of hydrochloric acid. It was calculated that at 93° C in the presence of 0.02 *N* acid, inversion was 99.99 percent complete in 16 minutes.

A solution was prepared in an Erlenmeyer flask containing 1.9665 g of sucrose, 78.2 ml of water, and 20 ml of 0.1 *N* hydrochloric acid. The position of the flask was so adjusted in the steam bath that the solution attained a temperature of 92° C in about 7 minutes. It was allowed to remain in the bath for an additional 23 minutes, during which time the temperature remained between 92° and 94° C. The solution was cooled, neutralized carefully with sodium hydroxide (brom-cresol green), and made up to a volume of 500 ml. The average of five analyses showed that 50 ml of this solution containing 207 mg of invert sugar precipitated 375.0 mg of copper. On the other hand, 207 mg of pure synthetic invert sugar precipitated 375.6, as shown by the mean of four determinations. Evidently Munson and Walker's high values for invert sugar are not due to the greater reducing power of hydrolyzed sucrose. The explanation of their excessive precipitations will be discussed in a later paragraph.

The deficiency in reducing power of sucrose hydrolyzed at a high temperature is in harmony with our measurements of the rotatory powers of invert sugar prepared by hydrolysis of sucrose [6]. We endeavored to show that the rotation of invert sugar is a function of the temperature at which the inversion is carried out, and the higher the temperature of inversion the greater the decomposition of invert sugar, even when the time of inversion is carefully chosen to avoid decomposition of the reaction products. Hence, to prepare a standard invert sugar solution from sucrose, elevated temperatures of inversion must be avoided.

Table 1 shows the reducing power of invert sugar prepared under various conditions of inversion. Each solution was prepared by inverting 1.9665 g of sucrose and making up to a final volume of 500 ml. A 50-ml aliquot contained 207 mg of invert sugar. The acid in each preparation was neutralized with sodium hydroxide, yielding small amounts of sodium chloride. Parallel experiments with mixtures of invert sugar and as much as 500 mg of sodium chloride showed that the salt had a negligible influence on the weight of copper reduced. As appears from the tabulated values, standard invert sugar solutions having the same reducing power as pure synthetic invert sugar can be prepared by room-temperature inversion. If the inversion is carried out at higher temperatures, a slightly diminished reducing power results.

TABLE 1.—*Reducing power of 207 mg of invert sugar prepared from sucrose*

Temperature of inversion	Acidity	Time of inversion	Volume of solution containing 1.9665 g of sucrose	Copper reduced
°C		hr	ml	mg
93	0.02 *N* HCl	0.5	100	375.0
76	.01 *N* HCl	3.2	11	374.8
55	.1 *N* HCl	4	11	374.9
24	.65 *N* HCl	70	100	375.5
23	1.0 *N* H_2SO_4	50	50	375.7
Synthetic invert sugar				375.6

For the inversion at laboratory temperature the procedure of Lane and Eynon [7] is suitable. "A solution of 9.5 g of pure sucrose is treated with 5 ml of hydrochloric acid (sp. gr. 1.19) made up to about 100 ml, left at room temperature for about a week at 12° to 15° or 3 days at 20° to 25° C and then made up to 1 liter. A known volume of the standard solution is neutralized with sodium hydroxide and suitably diluted immediately prior to use."

In the present series 3.933 g of sucrose was dissolved in 87.5 ml of water and acidified with 10 ml of 6.34 *N* hydrochloric acid (Clerget acid). It was allowed to stand at 23.5° to 24.5° C for 71 hours and was then neutralized with sodium hydroxide and made to a volume of 1 liter. Fifty milliliters of this solution contained 207 mg of invert sugar and 185 mg of sodium chloride.

2. DETERMINATION OF REDUCED COPPER

(a) CUPROUS OXIDE METHOD

Munson and Walker determined the precipitated copper by directly weighing the cuprous oxide and converting to metallic copper by the stoichiometrical factor. They stated that the method had been checked against the electrolytic and the thiosulfate methods and the accuracy of the cuprous oxide procedure demonstrated. The applicability of this stoichiometrical factor has been extensively debated in subsequent literature and apparently agreement has been reached that, while cuprous oxide is a true measure of copper in the analysis of pure sugars, it is unreliable for the analysis of crude substances because of the likelihood of contamination by impurities derived from the substance undergoing analysis. This was demonstrated by Sherwood and Wiley [8] in an extended series of analyses.

In an effort to explain the source of the considerable discrepancies between Hammond's and Munson and Walker's copper values, we duplicated Munson and Walker's cuprous oxide procedure in detail, and in addition determined the true reduced copper by thiosulfate titration or by electrolysis.

A series of platinum Gooch crucibles was available which had very fine perforations and held the asbestos with but negligible loss during analysis. The asbestos was prepared by the method of Brewster and Phelps [9]. The analytical results are shown in table 2, each figure in the table representing the mean of at least four analyses. In every instance but one the copper calculated from the cuprous oxide is higher than the true copper as shown by thiosulfate titration or electrolysis. Thus even with pure sugars the cuprous oxide is contaminated with organic decomposition products.

TABLE 2—*Contamination of cuprous oxide*

Weight of sugar	Cuprous oxide	Copper		
		by factor	by electrolysis	by thiosulfate
mg	*mg*	*mg*	*mg*	*mg*
207 (Invert, synthetic)	423.8	376.4	376.0	375.7
207 (Invert, sucrose)	424.7	377.2	----------	375.5
117 (Dextrose)	258.5	229.6	----------	229.7
207 (Dextrose)	438.1	389.1	388.1	388.0
207 (Levulose)	412.3	366.3	364.5	----------
207 (Invert, plus 1.793 g of sucrose)	439.3	390.2	385.7	385.7

The cuprous oxide from 207 mg of invert sugar prepared from sucrose shows from table 2 a contamination of 1.7 mg. The difference between Hammond's and Munson and Walker's copper is 1.8 mg. The cuprous oxide from 2.0 g of total sugar containing 207 mg of invert sugar has a contamination of 4.5 mg, while Hammond differs from Munson and Walker by 4.7 mg. A similar comparison of the dextrose values fails because Hammond obtained more copper than Munson and Walker. The average contamination of all the cuprous oxide precipitates in table 2 is 1.6 mg, while the average difference between Hammond and Munson and Walker in 46 analyses is 1.8 mg. In other words, it appears highly probable that the entire difference between the two series of analyses is due to the fact that Munson

and Walker's cuprous oxide was contaminated by appreciable quantities of organic decomposition products.

It is of interest to inquire why a so easily demonstrable contamination has not been revealed before. It is doubtless due to the fact that in most instances the comparison has been made with dextrose, which alone among the sugars causes a negligible contamination, at least at median concentrations of sugar. Thus up to a concentration of 180 mg of sugar Hammond differs from Munson and Walker by an average of only 0.2 mg of copper. In table 2, 117 mg of dextrose produced an uncontaminated precipitate, but the contamination became appreciable at 207 mg of sugar.

The conclusion seems justified that Munson and Walker's tables, so far as they relate sugar to metallic copper, are in error by the amount of the contamination. The apparent cuprous oxide-sugar equivalents are probably substantially correct if the amount of contamination is a constant quantity. This constant relation will hold in general for relatively pure sugars, but will fail for crude substances. On the other hand, Hammond's electrolytic copper is uncontaminated, but he has introduced into his tables the calculated weights of cuprous oxide. These latter values lead to erroneous results when cuprous oxide is weighed for the very reason that they are not contaminated.

It seems highly advisable that all reducing-sugar analyses be referred to metallic copper. We have therefore in the following paragraphs given attention to the analytical methods for the estimation of copper.

(b) THIOSULFATE METHOD

The iodometric determination of copper, when conducted under conditions insuring complete reduction of copper, is capable of an accuracy comparable to that of the best volumetric methods. The reaction on which the method depends, namely $2\,CuI_2 \rightarrow 2\,CuI + I_2$, is reversible; but if precautions are taken to remove cuprous ions as completely as possible and to maintain a sufficient concentration of iodide ions, the reaction runs quantitatively from left to right within the errors of measurement. Under suitable conditions the reaction can be made to run quantitatively from right to left. Shaffer and Hartmann [10] have shown that this, the cuprous titration, can be applied directly to the Munson and Walker method, but such a procedure causes a divergence from the specified routine of the method and will not be considered here.

Shaffer and Hartmann [10] studied the equilibria involved and showed that for amounts of copper up to 318 mg per 100 ml the final concentration of potassium iodide must be 4.2 g (or more) in 100 ml at the end of the titration. For greater amounts of copper the concentration of potassium iodide must be greater in direct proportion.

In the analyses reported here the volume of the copper solution was so adjusted by previous calculation and marking the Erlenmeyer flask that the volumes of the potassium iodide solution, thiosulfate, starch, and washings made the proper final concentration of potassium iodide. For the lowest concentration of copper the final concentration of potassium iodide was 2.1 g in 50 ml; for the highest (425 mg), 6.7 g in 115 ml.

Foote and Vance [11] have shown that the sharpness of the end point and the precision of analysis are enhanced by the addition of

ammonium thiocyanate at the approximate end point of the thiosulfate titration. Since cuprous thiocyanate is more insoluble than cuprous iodide, the thiocyanate has the effect of more completely removing cuprous ions from the solution and thus furthering the reaction from left to right. Another important result of the addition of thiocyanate is that apparently the surface portions of the precipitated cuprous iodide are converted to cuprous thiocyanate and the small quantity of adsorbed iodine is released to react with the thiosulfate. At the end point the precipitate is white, whereas without the thiocyanate it is slightly purple.

Although, as shown by Whitehead and Miller [12], the effect of small concentrations of strong acids is not considerable, that of acetic acid is even smaller. In our experience the reliability of the analysis is increased when the titration is carried out in the presence of acetic acid.

In reducing-sugar analysis the cuprous oxide is dissolved in 5 ml of 1:1 nitric acid. It has been the practice to neutralize the excess of nitric acid with sodium hydroxide and then add a few drops of acetic acid. This procedure is tedious and, as will be shown, unnecessary. The same object could be accomplished by adding a sodium acetate solution, if the acetic acid which is released has no appreciable effect on the titer. A 1:1 solution of nitric acid is about 8.3 *N*. Five milliliters of this solution would be completely buffered by 10 ml of a 4.22 *N* solution of sodium acetate. A maximum of 2.4 ml of acetic acid is released by the prescribed volumes of nitric acid and sodium acetate. The data showing that the effect of this procedure is inappreciable are given in table 3. The results must be considered merely comparative because the same figures are used to standardize the thiosulfate.

Of a pure copper sulfate solution 50-ml portions were titrated with 0.1573 *N* thiosulfate (1 ml = 10 mg of Cu) to a final volume of about 100 ml, 2 g of thiocyanate being added near the end of the titration.

TABLE 3.—*Effect of acetic acid on the thiosulfate titer*

Reagent	Number of analyses	Copper
		mg
0.1 ml of acetic	7	318.8
2 ml of acetic	5	318.8
5 ml of acetic	1	318.7
5 ml of 1:1 nitric + 10 ml of sodium acetate[a]	3	318.7

[a] This mixture releases 2.37 ml of glacial acetic acid.

In order to assure ourselves that the ratio of thiosulfate to copper was constant with both large and small amounts of copper, the series of analyses of a copper sulfate solution was made with the results shown in table 4. To each solution were added 5 ml of 1:1 nitric acid and 6 ml of 8 *N* ammonium acetate. The analyses showing the greatest departure from the mean, namely the second, third, and fifth, were in error by 0.01, 0.01, and 0.02 ml, respectively.

TABLE 4.—*Constancy of the ratio of thiosulfate to copper covering the range of volumes used in the determinations*

Volume of copper sulfate	Volume of final solution	Weight of potassium iodide	Titer	Ratio: thiosulfate to copper sulfate
ml	*ml*	*g*	*ml*	
15.026	54	2.2	12.634	0.8408
20.094	64	2.6	16.884	.8403
25.042	74	3.0	21.070	.8414
33.895	93	3.4	28.502	.8409
45.455	116	4.8	38.244	.8414
50.004	127	5.7	42.039	.8407
58.937	144	6.3	49.562	.8409
Average				0.8409

Procedure.—Collect the reduced copper on a Gooch crucible and wash the beaker and precipitate free from unreduced copper. From a 5-ml pipette add a few drops of 1:1 nitric acid to the reaction beaker and drop the remainder carefully on the precipitate, covering the crucible closely with a watchglass. Rinse the pipette and watchglass, catching the rinsings in the beaker. Allow the cupric nitrate and washings from the beaker to drain into an Erlenmeyer flask. Remove the nitrogen oxides by prolonged digestion on the steam bath or follow the usual procedure, using bromine water [13].

Cool and add 10 ml of sodium acetate solution (574 g of trihydrate per liter). Add a volume of potassium iodide solution (40 g per 100 ml) such that at the end of the titration the concentration of potassium iodide shall be 4.0 to 4.5 g per 100 ml. The potassium iodide should be added slowly and with continuous agitation.

Titrate with 0.1573 *N* thiosulfate, preferably adding the solution at the rate of about 13 ml per minute. Add a starch solution when the iodine color approaches disappearance and continue the titration until the blue starch iodide is just decolorized. Add about 2 g of ammonium thiocyanate and agitate until the salt is completely dissolved. Continue the titration to the disappearance of the blue color.

Standardize the thiosulfate (39 g of crystals per liter=0.1573 *N*) by titration against 0.2 to 0.4 g of pure copper dissolved in 5 ml of 1:1 nitric acid and treated as described for the cuprous oxide or against a measured volume of a copper sulfate solution which has been analyzed by electrolysis. In the latter case add 2 ml of acetic acid before titration. One milliliter of thiosulfate should be equivalent to approximately 10 mg of copper.

(c) PERMANGANATE METHOD

The original method of determining cuprous oxide by means of permanganate was devised by Mohr [14], who dissolved the precipitate in acidified ferric sulfate and titrated the resulting ferrous iron with permanganate which had been standardized against sodium oxalate. It was eventually discovered that the results were from 1 to 2 percent too low. Schoorl and Regenbogen [15] modified the method by dissolving the cuprous oxide in neutral ferric sulfate, subsequently acidifying and titrating. The modification has apparently eliminated the errors of the original method. The analytical results here reported substantiate this conclusion.

In this investigation the method of Schoorl and Regenbogen was used with but one essential modification. For the purpose of oxidizing reducing impurities in the stock ferric sulfate solution, the procedure has been to treat the neutral solution with an amount of permanganate determined by titration of an acidified sample. This seems a doubtful expedient because, as is well known, permanganate behaves differently in acid and alkaline (or neutral) solution. The procedure now recommended is to titrate 50 ml of the ferric sulfate solution, acidified exactly as in the analytical process, and to use the determined titer as a zero-point correction. This has the added advantage that the small excess of permanganate which is required to produce the color change and which in general will be approximately the same in the analysis is included in the correction.

Standardization.—[16] Prepare a solution, approximately 0.1573 *N*, containing 4.98 g of potassium permanganate per liter. After several days' aging, filter through asbestos or fritted glass.

Transfer 0.35 g of pure sodium oxalate (dried at 103°C) to a 600-ml beaker. Add 250 ml of sulfuric acid (1 volume of acid diluted with 19 volumes of water) previously boiled for 10 minutes and cooled to 27° C±3°. Stir until the oxalate is dissolved. Add 29 to 30 ml of permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Allow the mixture to stand until the pink color disappears (about 45 seconds). Heat to 55° or 60° C and complete the titration by adding permanganate dropwise until a faint pink color persists for 30 seconds. Allow each drop to become decolorized before adding the next.

Determine the excess of solution (usually 0.03 to 0.05 ml)required to impart the same pink color to the same volume of acid boiled and cooled to 55° to 60° C.

Weight, in grams, of oxalate×948.7÷titer=mg of copper per ml.

An equally satisfactory standard is arsenious oxide [17].

Ferric sulfate.—Dissolve 135 g of ferric ammonium alum or 55 g of ferric sulfate (anhydrous) and dilute to 1 liter. The ferric sulfate dissolves very slowly. Determine $Fe_2(SO_4)_3$ in the stock supply by strong ignition to Fe_2O_3. Acidify 50 ml with 20 ml of 4 *N* sulfuric acid and titrate with permanganate to the slightest perceptible color change. Apply the titer (usually 0.03 to 0.08 ml) as a zero-point correction in analytical titrations.

Determination.—[13] Filter the cuprous oxide on a Gooch crucible and wash the beaker and precipitate thoroughly. Transfer the asbestos film to the beaker with the aid of a glass rod. Add 50 ml of the ferric sulfate solution and stir vigorously until the cuprous oxide is completely dissolved. Examine for complete solution, holding the beaker above the level of the eye. Add 20 ml of 4 *N* sulfuric acid and titrate with standard permanganate to the same color change as in the titration for zero-point correction.

The end point is rendered sharper by the addition of one drop of ferrous phenanthroline indicator (0.7425 g of orthophenanthroline monohydrate in 25 ml of 0.025 *M* ferrous sulfate).

Discussion.—The permanganate method as modified by Schoorl and Regenbogen yields highly accurate results. It is eminently suitable for small amounts of cuprous oxide and has indeed found its greatest serviceability for such small amounts that the titration can be carried out with 0.033 *N* permanganate. When larger amounts of cuprous oxide (from 200 to 400 mg) are precipitated, great difficulty

is encountered in dissolving the precipitate. In many of the analyses reported here, a period of 45 minutes was required before the cuprous oxide was dissolved. Table 5 shows some of the analytical results obtained.

TABLE 5.—*Comparative analyses by permanganate and thiosulfate*

Substance	Copper by permanganate	Number of analyses	Difference between extremes	Copper by thiosulfate	Number of analyses	Difference between extremes	Difference permanganate minus thiosulfate
mg	*mg*		*mg*	*mg*		*mg*	*mg*
69 Invert	133.12	4	0.89	133.29	5	0.67	−0.17
220 Invert	396.82	3	.39	397.08	3	.51	−.26
184 Dextrose	349.62	4	.70	349.35	4	.69	+.27

(d) DICHROMATE METHOD

In a previous article Jackson and Mathews [4] described a method by which cuprous oxide was dissolved in an excess of acidified potassium dichromate and titrated back to an electrometric end point with ferrous sulfate. Since the advent of the indicator, orthophenanthroline [18], the same titration can be made colorimetrically. Some modification of the method is necessary because, whereas the electrometric titration can be made in 1.2 *N* acid, the colorimetric procedure requires that the final solution be about twice normal in hydrochloric acid. Below this acid concentration the end point is uncertain and slow of attainment.

The colorimetric and electrometric end points do not occur at exactly the same titer of ferrous sulfate. On back titration the color change occurs first and the large potential change when an additional 0.02 ml (in average) of 0.1573 *N* ferrous sulfate has been added.

All of the earlier electrometric measurements were made with an instrument constructed in the laboratory, similar to the one described by Forbes and Bartlett [19]. The later measurements were made with a Serfass Electron-Ray Titrimeter [20]. Comparative analyses showed that the earlier instrument had served satisfactorily.

The dichromate method is the most expeditious for determining copper. The cuprous oxide dissolves readily in the hydrochloric acid-dichromate solution, in contrast to the difficulty of dissolving in ferric sulfate. In precision it approaches the thiosulfate method very closely at the median and lower concentrations of sugar. At the high concentrations of sugar the results are from 0.1 to 0.2 percent lower. The method would appear particularly serviceable when a considerable number of analyses are required quickly.

Reagents.—Standard dichromate solution, 0.1573 *N* (containing 7.7135 g of crystals of pure potassium dichromate dried at 150° C in 1 liter). One milliliter of this solution is equivalent to 10 mg of copper.

Approximately 6 *N* hydrochloric acid.

Ferrous ammonium sulfate solution, containing 61.9 g of the hexahydrate and 5 ml of concentrated sulfuric acid in 1 liter.

Phenanthroline-ferrous complex. Dissolve 0.7425 g of orthophenanthroline monohydrate in 25 ml of 0.025 *M* ferrous sulfate solution (6.95 g of $FeSO_4 \cdot 7H_20$ in 1 liter).

Procedure. –Estimate the volumes of dichromate, ferrous sulfate, hydrochloric acid, and water which will give an assured excess of dichromate and yield a concentration of about 2 *N* acid in about 200 ml of final volume. An error of 5 percent, or in most cases even 10 percent, in acid concentration, can be tolerated. Fill graduated cylinders with the required volumes of water and acid.

Collect the precipitated cuprous oxide on a Gooch crucible and wash thoroughly. Detach the mat with a glass rod and transfer to the reaction beaker. Add a small volume of water and disintegrate the mat. Pipette accurately a volume of standard dichromate in excess of the quantity required to oxidize the cuprous oxide. In general the approximate weight of copper will be known or can be roughly estimated, but in any case a sufficient volume must be added to supply an assured excess. Add rapidly the whole required volume of hydrochloric acid with continuous stirring and continue to stir until all the cuprous oxide is dissolved. Immerse the crucible in the solution and be assured that the adhering cuprous oxide is dissolved. Remove the crucible with the glass rod and wash it with the water from the graduate. Add one drop of phenanthroline solution and titrate with ferrous sulfate to the permanent appearance of the brown ferrous-phenanthroline complex. As the end point is approached, the brown color appears and fades as each of the last few drops is added; and the ferrous sulfate must be added until the color is permanent, the additions finally being in fractions of drops.

Determine the ratio of concentrations of ferrous sulfate and dichromate and from this ratio compute the volume of dichromate required for the oxidation of cuprous oxide. This volume multiplied by 10 gives directly the number of milligrams of copper reduced.

The titration can be conducted electrometrically, in which case the addition of the indicator is unnecessary. Both colorimetric and electrometric end points can be determined in the same solution.

3. THE REDUCTION REACTION

The reduction reaction was conducted in rigorous accordance with Munson and Walker's specifications. The analyses were made in 400-ml beakers covered with watchglasses. The solutions were brought to the boiling point in about 4 minutes by a previous adjustment of conditions. When a solution approached the boiling point, there usually occurred a few sporadic periods of apparent boiling which were followed by a very definite moment when the whole solution suddenly started to boil vigorously. This latter appearance was taken as the starting time of the 2-minute period. It was found important that the beakers after use be allowed to dry on a rack for at least 1 day and preferably several days. If they are thoroughly aerated in this way, the time of boiling can be definitely recognized and no superheating or bumping occurs.

Since at the expiration of the 2-minute period of boiling the solutions remain approximately at the boiling temperature, it is important that the time required for filtration be uniform. By adjusting the vacuum and the thickness of the asbestos mat, the rate of filtration was roughly controlled so that 30 to 50 seconds elapsed between the end of the boiling period and the completion of the filtration. Naturally in

many analyses the time varied from this standard and such variations probably contributed to the error of analysis, but in most instances imperceptibly.

Blank determinations were made of the amount of copper precipitated by boiling the mixed reagents without addition of sugar and collecting the precipitate on a Gooch crucible. This was moistened with 1:1 nitric acid, washed into a flask, and evaporated to dryness. The residue was dissolved in 0.25 ml of acetic acid, transferred to a test tube, and made up to 5 ml with water. A drop of potassium ferrocyanide was added, and the sample was compared colorimetrically with standards containing known weights of copper. Quite uniformly throughout the investigation this blank test showed 0.3 mg of copper, with maximum deviations of less than 0.05 mg. Munson and Walker [1] determined the copper reduced in blank experiments by weighing cuprous oxide. The average value from 67 determinations was 0.24 mg of copper. They obtained many blanks of negative value. If these are rejected, together with the equally improbable ones of 1 mg or more, their average is 0.33 mg. Both of these averages are in essential agreement with the values found in our analyses.

The copper reduced by the reagents is caused by the oxidizing effect of cupric copper on the alkaline tartrate. The amount of reduction probably varies with the concentration of copper and would not be the same if much of the copper is rapidly reduced by sugar. It therefore seems a questionable procedure to apply a uniform blank correction to all analyses regardless of the concentration of sugar. Moreover, the analyst who uses the empirical tables seldom determines or applies a blank correction, and for his purpose the uncorrected tables are more directly applicable. For these reasons we shall in the following pages report the weights of copper precipitated by sugar exactly as determined without application of a blank correction. This procedure is in harmony with that of Hammond, who published the copper values obtained without correction for blanks.

The foregoing statements apply to Soxhlet reagents that are not more than a few months old. After long standing, the blank becomes increasingly greater. If the analyst determines a blank correction and finds a value different from 0.3 mg, he has merely to deduct all but 0.3 mg from his copper precipitate in order to be in correspondence with Hammond's or our data.

III. EXPERIMENTAL RESULTS

By the methods which have been described, analyses were made of the three sugars, dextrose, levulose, and invert sugar at 10 concentrations ranging from 23 to 230 mg in 50 ml of solution. At each concentration usually eight determinations were made, in four of which the reduced copper was determined by thiosulfate titration and in the remaining four by colorimetric dichromate titration.

The results of the analyses of dextrose solutions are shown in table 6. The experimental results for the thiosulfate analysis of copper (column 2) were correlated by the method of least squares, the computation yielding the formula

$$\text{Cu (by thiosulfate)} = 2.0820\, d - 0.001005\, d^2, \qquad (1)$$

in which copper and dextrose (d) are expressed in milligrams. The residuals (column 4) are satisfactorily small.

It is of interest to compare this series of analyses with a series completed and published [21] previously in which the copper was related to the dextrose by the formula

$$\text{Cu (by thiosulfate)} = 2.0800\ d - 0.000989\ d^2. \quad (2)$$

The two independent series show no deviation (column 6) as great as 1 part in a thousand. For tabulation, the mean of these two formulas will be taken as the best result of this investigation:

$$\text{Cu (by thiosulfate)} = 2.0810\ d - 0.000997\ d^2. \quad (3)$$

TABLE 6.—*Milligrams of copper reduced by dextrose*

Weight of dextrose	Copper by thiosulfate					Copper from Hammond's table	Difference of mean [e] from Hammond's table		Copper by dichromate (colorimetric)			
	Series II			Calculated [b] from Series I	Series II minus series I (calculated)							
	Found	Calculated [a]	Found minus calculated						Found	Calculated [d]	Found minus calculated	Dichromate minus thiosulfate (calculated values)
mg							*mg*	*percent*				
23	46.3	47.3	−1.0	47.3	0	47.8	−0.5	1.0	46.8	47.3	−0.5	−0.0
46	94.0	93.7	+0.3	93.6	+0.1	94.0	−.4	0.4	94.3	93.5	+.8	−.1
69	138.6	138.9	−.3	138.8	+.0	139.0	−.2	.1	138.3	138.7	−.4	−.1
92	183.2	183.0	+.2	183.0	0	183.0	0	0	182.7	182.8	−.1	−.2
115	225.9	226.1	−.2	226.1	0	225.8	+.3	.1	225.6	225.8	−.2	−.3
138	268.0	268.2	−.2	268.2	0	267.6	+.6	.2	268.0	267.8	+.2	−.4
161	309.3	309.2	+.1	309.2	0	308.5	+.7	.2	308.5	308.7	−.2	−.5
184	349.1	349.1	0	349.2	−.1	348.3	+.8	.2	348.9	348.5	+.4	−.7
207	388.3	387.9	+.4	388.2	−.3	387.2	+.8	.2	387.2	387.3	−.1	−.9
230	425.4	425.7	−.3	426.1	−.4	424.8	+1.1	.3	425.0	425.0	0	−1.1

[a] Formula 1, Cu (by thiosulfate) = $2.0820\ d - 0.001005\ d^2$.
[b] Formula 2, Cu (by thiosulfate) = $2.0800\ d - 0.000989\ d^2$.
[c] Formula 3, Cu (by thiosulfate) = $2.0810\ d - 0.000997\ d^2$ (mean of 1 and 2).
[d] Formula 4, Cu (by dichromate) = $2.0792\ d - 0.001005\ d^2$.

In the last four columns of table 6 are shown the results of the analysis by colorimetric dichromate titration. A least-square computation yielded the formula

$$\text{Cu (by dichromate)} = 2.0792\ d - 0.001005\ d^2. \quad (4)$$

In the low and medium ranges of concentration the dichromate titrations agree essentially with the thiosulfate values for total copper, but in the higher concentrations the dichromate values fall slightly below those by thiosulfate, the discrepancy rising to a maximum of 0.26 percent. This difference occurs not only for dextrose but also, as will appear below, for levulose and invert sugar. It cannot therefore be ascribed to analytical error, but must be explained by some more fundamental property of the reaction which was not further investigated.

In the article previously cited [21] a series of dichromate-dextrose equivalents was published. These are not directly comparable with those given in table 6 because they were determined by electrometric titration at a hydrochloric-acid acidity of about 1.2 to 1.4 *N*. Systematic experimentation showed a consistent difference of 0.06 ml of dichromate between the electrometric end point in the presence of 1.2

N hydrochloric acid, and the colorimetric end point in 2 N hydrochloric acid, whereas the mean experimental difference between the two respective series of sugar analyses proved to be 0.054, the electrometric titration giving in both cases the lower volume of dichromate. The two series of analyses thus yielded consistent results.

In table 7 are assembled the data on the reducing action of levulose. Least-square computations yielded the respective formulas

$$\text{Cu (by thiosulfate)} = 1.8818\ l - 0.000596\ l^2 \quad (5)$$

and

$$\text{Cu (by dichromate)} = 1.8840\ l - 0.000614\ l^2. \quad (6)$$

TABLE 7.—*Milligrams of copper reduced by levulose*

Weight of levulose	Copper by thiosulfate			Copper from Hammond's table	Difference from Hammond's table (calculated values)		Copper by dichromate (colorimetric)			
	Found	Calculated [a]	Found minus calculated				Found	Calculated [b]	Found minus calculated	Dichromate minus thiosulfate (calculated values)
mg					*mg*	*percent*				
23	43.3	43.0	+0.3	43.4	−0.4	1.0	43.7	43.0	+0.7	0
46	85.5	85.3	+.2	85.8	−.5	0.6	85.2	85.4	−.2	+0.1
69	126.9	127.0	−.1	127.4	−.4	.3	127.4	127.1	+.3	+.1
92	168.1	168.1	0	168.4	−.3	.2	168.2	168.1	+.1	0
115	208.5	208.5	0	208.7	−.2	.1	208.2	208.5	−.3	0
138	248.2	248.3	−.1	248.5	−.2	.1	248.3	248.3	0	0
161	287.6	287.5	+.1	287.5	0	0	287.1	287.4	−.3	−.1
184	326.2	326.1	+.1	326.0	+.1	0	325.9	325.9	0	−.2
207	363.9	364.0	−.1	363.8	+.2	.1	363.6	363.7	−.1	−.2
230	401.5	401.3	+.2	400.9	+.4	.1	401.3	400.9	+.4	−.4
243	421.9	422.1	−.2	421.1	+1.0	.2	421.4	421.6	−.2	−.5

[a] Formula 5, Cu (by thiosulfate) = $1.8818l - 0.000596l^2$.
[b] Formula 6, Cu (by dichromate) = $1.8840l - 0.000614l^2$.

The small values of the residuals show that the formulas represent the data satisfactorily.

The reduction data on invert sugar are given in table 8. Least-square adjustment yielded the formulas

$$\text{Cu (by thiosulfate)} = 1.9834\ i - 0.000818\ i^2 \quad (7)$$

and

$$\text{Cu (by dichromate)} = 1.9828\ i - 0.000827\ i^2. \quad (8)$$

While the measurements were in progress, it was expected that the rule of mixtures would apply to the problem and that the copper reduced by invert sugar would be the mean of the amounts precipitated by dextrose and by levulose. Such proved not to be the case. The copper reduced by invert sugar is less than the mean by the two constituents (with the exception of the lower concentrations), the deficiency rising to somewhat more than 0.1 percent at the higher concentrations in the analysis by thiosulfate and to more than 0.2 percent in those by dichromate.

TABLE 8.—*Milligrams of copper reduced by invert sugar*

Weight of invert sugar	Copper by thiosulfate			Copper from Hammond's table	Difference from Hammond's table (calculated values)		Copper by dichromate			
	Found	Calculated [a]	Found minus calculated				Found	Calculated [b]	Found minus calculated	Dichromate minus thiosulfate (calculated values)
mg					*mg*	*percent*				
30	45.0	45.2	−0.2	45.2	0	0	45.2	45.1	+0.1	−0.1
86	89.3	89.5	−.2	89.6	−0.1	0.1	89.1	89.4	−.3	−.1
89	132.5	133.0	−.5	133.0	0	0	132.3	132.7	−.4	−.3
92	175.1	175.5	−.4	175.6	−.1	.1	175.5	175.3	+.2	−.2
115	217.3	217.3	0	217.2	+.1	0	217.0	216.9	+.1	−.4
138	258.1	258.1	0	258.0	+.1	0	257.3	257.7	−.4	−.4
161	298.4	298.1	+.3	298.0	+.1	0	298.1	297.5	−.4	−.6
184	337.2	337.2	0	337.0	+.2	.1	336.4	336.5	−.1	−.7
207	375.9	375.5	+.4	375.2	+.3	.1	374.9	374.7	+.2	−.8
230	412.7	412.9	−.2	412.4	+.5	.1	411.6	411.9	−.3	−1.0

[a] Formula 7, Cu (by thiosulfate) = $1.9834\,i - 0.000818\,i^2$.
[b] Formula 8, Cu (by dichromate) = $1.9828\,i - 0.000827\,i^2$.

The amount of copper reduced is a function not only of the concentration of sugar but also of the concentration of copper. If one constituent of a sugar mixture reacts upon the copper more rapidly than the other, it will diminish the copper concentration before the second constituent has reacted. The latter then will undergo reaction in a lower concentration of copper when in a mixture than when alone, and theoretically should reduce less copper [22]. This theory is completely in accord with the very exact results of Quisumbing and Thomas [23], whose deviations from the rule of mixtures are in the same direction and of about the same magnitude as those in this article.

The weight of copper precipitated in all methods in which the reduction is carried out at the boiling point is influenced by the barometric pressure. During the experiments described here a complete record of the barometric readings was kept. When a considerable change in pressure occurred, its effect was definitely noticeable in the amount of copper precipitated. In extreme cases the determination was repeated under more favorable atmospheric pressure conditions. The mean barometric reading for dextrose was 757 mm; for levulose, 756 mm; and for invert sugar, 752 mm (corrected to 0°C and for latitude).

The data in tables 6 to 8 permit an appraisal of the dichromate method. Compared with the thiosulfate method the results are slightly low. In the dextrose table there is an average deficiency of 0.14 percent; in the invert sugar table, of 0.19 percent; and in the levulose table, of 0.05 percent. The mean deficiency in all 31 analyses is 0.13 percent. If this difference should prove to be constant, it could readily be corrected empirically, most simply by diminishing the concentration of dichromate in the standard solution by 0.13 percent. The residuals would then have both positive and negative signs, and the errors would be of the order of 0.1 percent.

IV. COMPARISON OF DATA WITH THOSE OF HAMMOND

In tables 6, 7, and 8 are shown the deviations of the results from those of Hammond, the difference being given both in milligrams and in percentage of the copper reduced. A definite trend is noticeable, the results of the present measurements being in general slightly lower than Hammond's at the low concentrations of sugar and higher at the high concentrations. This suggests some small systematic difference in procedure. In conference it was revealed that Hammond's crucibles were probably more closely packed than the authors', thus causing a slight increase in the time required for filtration. Hammond required 90 to 100 seconds to filter the reaction mixture, while the authors required 30 to 50 seconds.

At the end of the 2-minute period of boiling there are two competing reactions which occur during the filtration. One is the back oxidation of cuprous oxide by air, resulting in re-solution of precipitated copper; the other is the continued reduction of copper. The additional amount of copper reduced by an extension of time of the reaction is dependent on the amount of sugar taken for analysis. Thus, as shown in table 9, the weight of reduced copper increases considerably with extension of time for low concentrations of dextrose, less so for intermediate concentrations, and not at all for high concentrations.

The slower filtration in Hammond's analyses is equivalent to a slight extension of reaction time. Hence at low concentrations of sugar he obtained, as expected, slightly greater reduction of copper. Throughout the wide range of intermediate concentrations these two competing effects counterbalance each other and the agreement between the two sets of analyses is highly satisfactory. In the range of the greater weights of sugar the only remaining effect of delayed filtration is the back oxidation by air, and thus Hammond obtained slightly less copper than the authors.

TABLE 9.—*Effect of duration of boiling on the amount of copper precipitated at varying concentrations of sugar*

Dextrose (mg)	46	138	230
Duration of boiling	Copper		
Minutes	*mg*	*mg*	*mg*
1	91.4	265.3	424.3
2	93.5	268.1	423.9
3	94.8	269.0	424.6
4.5	96.9	271.6	423.9
6	98.5	273.7	424.6

It would perhaps be possible to add more closely defined specifications for the Munson and Walker method. This appears inadvisable since it would detract from the simplicity of the method.

A comparison of these two investigations serves fairly to evaluate the precision obtainable by Munson and Walker's method, since they represent two quite independent series of analyses. The percentage deviations of the authors' values from those of Hammond are given in the respective columns of tables 6 to 8. Of the 31 values given, 19, or 61 percent, are in agreement within 0.1 percent, and 25, or 81 percent,

within 0.2 percent. The remaining six values are all at the extreme high or low concentrations of sugar. All the values for invert sugar and 6 of the 11 values for levulose agree within 0.1 percent. Curiously enough the deviations are greater in the dextrose analyses than in those of the other sugars. The mean difference from Hammond throughout the whole series of three sugars is, regardless of sign, 0.19 percent. The greater part of this difference is contributed by the extreme high and low concentrations of sugar.

Munson and Walker's procedure is essentially a macromethod. If, therefore, we confine our attention to those determinations where there is sufficient precipitation to insure accuracy, and not so great a precipitation that the copper approaches exhaustion, say between 69 and 207 mg of sugar, we find an average deviation from Hammond of 0.5 mg, or 0.17 percent, for dextrose; 0.2 mg, or 0.11 percent, for levulose; and 0.1 mg, or 0.05 percent, for invert sugar. The mean deviation for all three sugars within this range of concentration is 0.26 mg, or 0.11 percent.

It is probable that a close collaboration would result in a reconciliation of the small differences observed, but the value of such an attempt would be problematical. The conclusion seems justified that the copper equivalents found in the present investigation corroborate those of Hammond well within the limits of experimental error. We therefore recommend that Hammond's tables be substituted for those of Munson and Walker in all analyses where the reduced copper is determined analytically.

Of the sucrose-invert sugar mixtures, we have undertaken only a small number of analyses for verifying Hammond's data and assisting in making a decision between his data and those of Erb and Zerban [2]. These latter authors have established formulas relating copper to 0.4 g of mixtures of sucrose and invert sugar. At the higher concentrations of invert sugar they are in almost perfect agreement with Hammond, but at certain lower concentrations their values diverge by a maximum of 1.7 mg of copper. Since their discrepant values are in agreement with Munson and Walker's copper precipitates, which, as has been shown above, are contaminated, they are probably too high.

In table 10 are given the weights of copper obtained from various sucrose-invert sugar mixtures. Our values follow the general tendency found in the previous analyses, an agreement with Hammond at the middle range of concentrations and a slightly greater recovery of copper at the high concentrations. In the analysis of 0.4 g of total sugar our results are in practically perfect agreement with those of Hammond.

TABLE 10.—*Copper equivalents of some sucrose-invert sugar mixtures*

Total sugar	Sucrose	Invert sugar	By thiosulfate	By electrolysis	From Hammond's table	From Erb and Zerban's formula	By dichromate	
							Colorimetric	Electrometric
g	*g*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
2.0	1.880	120	.....	238.9	238.7	.....	238.8	238.6
2.0	1.793	207	385.6	384.7	384.2	.....	.....	.....
2.0	1.770	230	421.6	421.2	420.3	.....	.....	.....
0.4	0.340	60	156.4	.....	156.5	158.2	156.9	156.8
.4	.320	80	119.6	.....	119.7	121.3	.....	.....

V. SUMMARY AND CONCLUSIONS

In a recent revision of the Munson and Walker reducing-sugar tables [1] by Hammond [3], important deviations in many of the copper values were disclosed. The present investigation, constituting a third series of analyses, corroborates Hammond's measurements within the limits of experimental error. The differences between Hammond's and Munson and Walker's values for copper are due almost entirely to the respective methods of estimating copper. Hammond determined the reduced copper by electrolysis, whereas Munson and Walker weighed the precipitated cuprous oxide. It is now shown that the cuprous oxide is contaminated with organic decomposition products even when pure sugars are analyzed. The amount of contamination is almost exactly equal to the difference between Hammond's and Munson and Walker's copper values.

The authors have shown that reduced copper should be determined by analysis and not by direct weighing of cuprous oxide and that Hammond's tables should be substituted for those of Munson and Walker.

Erb and Zerban's analyses of 0.4 g of sucrose-invert sugar mixtures are in agreement with those of Hammond except within a short range of lower concentrations. The analyses here presented are in agreement with Hammond's within this range.

The various methods for the determination of copper are discussed. The main reliance during the investigation was the iodometric method in acetic acid solution, with the concentration (4.2 g per 100 ml) of potassium iodide specified by Shaffer and Hartmann [10], and with the addition of thiocyanate at the end of the titration as specified by Foote and Vance [11].

A method of determining cuprous oxide by oxidation with an excess of dichromate and back titration with ferrous sulfate to a colorimetric or electrometric end point is described.

The permanganate method as modified by Schoorl and Regenbogen [15] is shown to give accurate results.

The precision of Munson and Walker's method, as indicated by Hammond's and the authors' independent analyses, is shown to be about 0.2 percent. If the concentrations of sugar are restricted to the range between 69 and 207 mg of reducing sugar, the average precision appears to be about 0.1 percent.

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EVOLUTION OF CARBON DIOXIDE AND WATER FROM VEGETABLE-TANNED LEATHERS AT ELEVATED TEMPERATURES

By Joseph R. Kanagy

ABSTRACT

The rates of evolution of carbon dioxide and water from untanned-hide powder and from chestnut-, quebracho-, cutch-, and sumac-tanned leathers in the presence of oxygen or air or of one of the inert gases, nitrogen or helium, in the temperature range 60° to 140° C were determined. Hide powder evolves much less carbon dioxide and water than the leathers. Chestnut leather evolves carbon dioxide at the greatest rate, and the order of decreasing rate of evolution of carbon dioxide by the leathers is chestnut, sumac, cutch, and quebracho. Cutch and quebracho leathers in the presence of air and oxygen generally give off more water than sumac and chestnut leathers. The rates of evolution of carbon dioxide from all the leathers heated in the presence of oxygen or air increase in the majority of cases by a multiple of approximately 3 for every 20° C rise in temperature. The changes in the rates at which water is evolved under the same conditions are smaller. The ratio of carbon to hydrogen oxidized to carbon dioxide and water, respectively, is approximately 1 to 3. In the presence of helium, the amounts of carbon dioxide found are small, a fact which indicates that the mechanism of the reaction in oxygen is principally an oxidation. The ratios of the amounts of carbon dioxide and water produced in the presence of air to those amounts produced in the presence of oxygen are different from the ratio of the partial pressures of oxygen in the two gases. The amounts of carbon dioxide emitted from the leathers correlate linearly with the percentages of the total nitrogenous materials extractable by a 0.1 *N* solution of sodium carbonate from leathers treated under the same conditions.

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I. INTRODUCTION

The oxidation of vegetable tannins has been associated with the darkening of the colors of solutions and of materials containing tannin, with the difficulty in determining the moisture content of leather, and with the deterioration of vegetable-tanned leather in storage. J. Jany [1] [1] and E. W. Merry [2] measured the rates of absorption of

[1] Figures in brackets indicate the literature references at the end of this paper.

oxygen by tannins and assumed that these rates were proportional to the rates of oxidation. Merry [2] made a thorough study of the amounts of oxygen absorbed by tanning materials and by ordinary and treated tannin solutions.

The results obtained in a series of investigations at the National Bureau of Standards on the stability of vegetable-tanned leathers at elevated temperatures have been presented in previous papers [3, 4, 5]. In those investigations the change in stability of the leathers under the various conditions studied was determined from chemical changes occurring in the hide substance and from physical tests of the leather. In two of those papers [3, 4] it was shown that carbon dioxide and water were evolved from leathers in the presence of oxygen and that the rates at which carbon dioxide was evolved at a constant temperature varied directly with the rates of deterioration of the leathers when aged in oxygen under pressure. The deterioration of the leathers aged under these conditions was measured by the percentage of the total nitrogenous materials extractable by a 0.1 N solution of sodium carbonate.

In the present investigation a further study has been made of the amounts and rates of evolution of carbon dioxide and water from leathers at different temperatures and in the presence of different gases. The purpose was to obtain additional information which could be used in developing a suitable aging test for leather. This work, which involves principally changes occurring in the tannins, is correlated with other work in which chemical changes in the hide substance were studied.

II. APPARATUS AND PROCEDURE

The leathers used in this investigation were tanned in the experimental tannery at the National Bureau of Standards. Four types were prepared, namely, chestnut, quebracho (ordinary), cutch, and

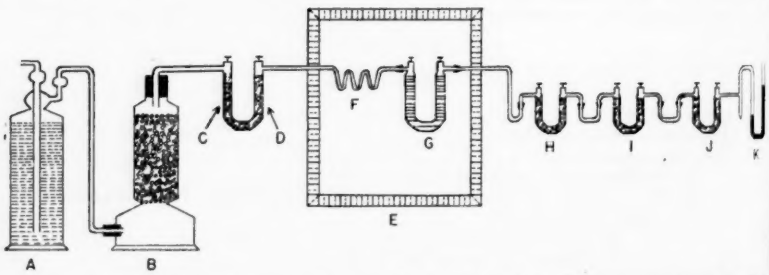

FIGURE 1.—*Diagram of apparatus used in determining the amounts of carbon dioxide and water evolved from leather.*

A, sulfuric acid; *B*, soda lime; *C*, Ascarite; *D*, magnesium perchlorate; *E*, oven; *F*, preheating coil; *G*, leather sample; *H*, water absorbed; *I*, carbon dioxide absorbed; *J*, safety tube; *K*, flowmeter.

sumac. These leathers were analyzed to determine their tannin contents, then degreased, and conditioned at 65-percent relative humidity and 70° F before the experiments were made.

A diagram of the apparatus used in making the experiments is shown in figure 1. Samples of the leathers, each weighing approximately 5 g, were placed in U-tubes equipped with side arms having ground-glass connections. The U-tubes were placed in the oven and connected to

the gas train, as shown in the figure. The temperature of the oven was maintained constant within $\pm 1.5°$ C. A continuous stream of either dry oxygen, air, or one of the inert gases, helium or nitrogen, was passed over the samples, then led outside the oven and through a series of U-tubes. The water evolved was absorbed in anhydrous magnesium perchlorate in the first U-tube and the carbon dioxide was absorbed in Ascarite in the second U-tube. The rates of evolution of these gases were determined by weighing the U-tubes at regular intervals. The rate of flow of the gas stream was 8 to 12 cm^3 per minute.

III. EXPERIMENTAL RESULTS

The amounts and rates of evolution of carbon dioxide and water from leathers tanned with chestnut, quebracho, cutch, and sumac, when heated at 60°, 80°, 100°, 120°, and 140° C in the presence of oxygen or air, or of one of the inert gases, helium or nitrogen, were measured. No study of the rates of evolution of carbon dioxide or water was made below 60° C because this was the lowest temperature at which measurable quantities of carbon dioxide were evolved in short periods of time. The study was not continued above a temperature of 140° C because at this point small quantities of organic materials condense on the cold walls of the glass tubing, just outside of the oven, an indication that a breakdown, other than the formation of carbon dioxide and water, began at this temperature. The experiments made possible not only determinations of the rates of evolution of carbon dioxide and water at a constant temperature but also permitted determinations of the increases in the rates of evolution of these gases with increase in temperature.

1. STUDIES WITH CHESTNUT-TANNED LEATHER

The amounts of carbon dioxide and water evolved from chestnut leather heated in oxygen are shown in figure 2. Each curve represents the amount evolved, during the specified time at the specified temperature expressed as a percentage of the weight of the tanned leather. At all temperatures the evolution of carbon dioxide and water is most rapid during the first 4 or 5 days. After this the rate decreases slowly with increase in time. The rates of evolution are greatest at higher temperatures, particularly above 100° C. The curves showing the rate of evolution of water have been arbitrarily extrapolated to 14.6 percent. This value is very close to the values obtained by the usual method of determining the water content of leathers, namely, drying at 100° C in the presence of air for 16 hours, and may be assumed to be that water reversibly adsorbed by the leather. Values above 14.6 percent are considered to be water resulting from oxidation or dehydration reactions. It may be noted in the figure that only one point, that representing a percentage evolved at 60° C, is lower than this percentage for the adsorbed water.

When chestnut leather was heated in the presence of air at different temperatures, the trends with regard to the rates of evolution of carbon dioxide and water were similar to those shown when it was heated in oxygen. However, much smaller amounts of the two gases were produced. The amount of carbon dioxide evolved from chestnut leather in the presence of air at any temperature was approximately one-half of that evolved in the presence of oxygen.

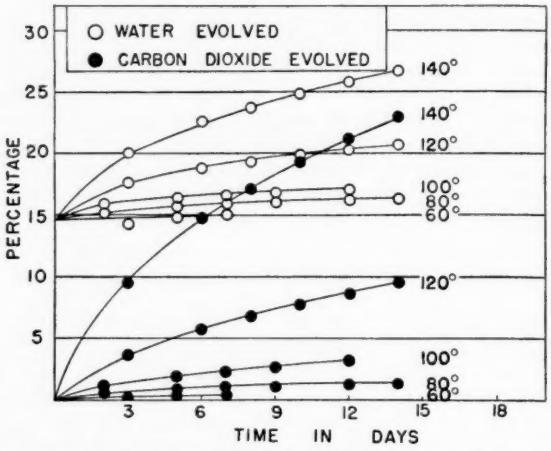

FIGURE 2.—*Rates of evolution of carbon dioxide and water from chestnut-tanned leather heated in oxygen at various temperatures.*
Percentages are based on the weight of the conditioned leather.

Carbon dioxide and water evolved in the presence of helium may be considered to originate from direct decomposition. That the amounts coming from this source are very small is shown by figure 3, where the amounts of carbon dioxide and water evolved from chestnut leather when heated at 120° C in the presence of either oxygen, air, or helium are recorded.

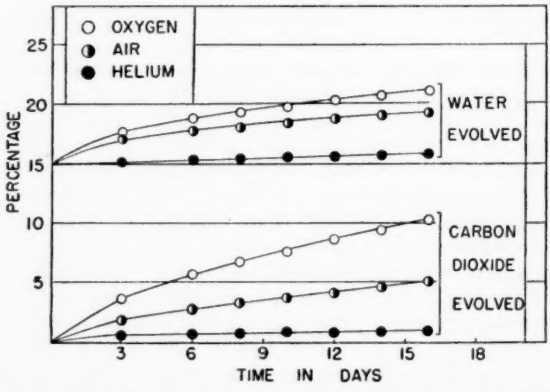

FIGURE 3.—*Rates of evolution of carbon dioxide and water from chestnut-tanned leather heated at 120° C in the presence of either oxygen, air, or helium.*
Percentages are based on the weight of the conditioned leather.

2. RATES OF EVOLUTION OF CARBON DIOXIDE AND WATER FROM VEGETABLE-TANNED LEATHERS

The method originally used in making the studies with chestnut leather required considerable time because it was necessary to continue the experiments for 2 weeks and to change samples for each experiment. A new method was therefore introduced in which one sample

of leather was used throughout the entire range of temperatures and the time of heating at any one temperature was reduced to 7 days. Thus a sample was heated at 60° C for 1 week. At the end of this period the temperature was raised to 80° C and the same sample heated for another week. This procedure was repeated at 20-degree intervals throughout the range of temperatures studied. These results are recorded in figure 4, where the percentages of carbon dioxide evolved at different intervals at the specified temperatures are given. At each temperature the rate of evolution of carbon dioxide was first rapid, after which it slowly diminished. This is similar to the result

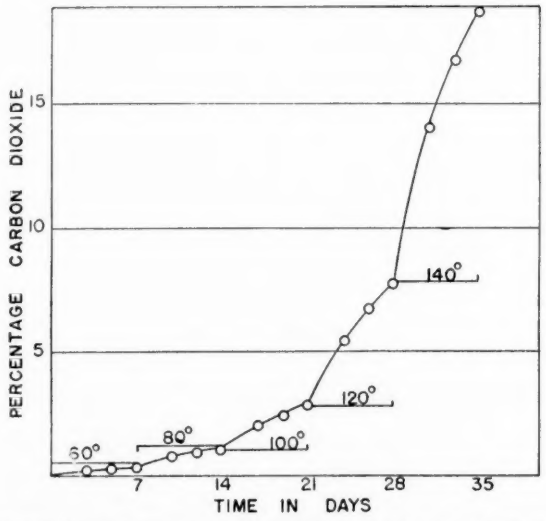

FIGURE 4.—*Evolution of carbon dioxide from a single sample of chestnut-tanned leather heated for 35 days, 7 days at each indicated temperature.*
Percentages are based on the weight of the conditioned leather.

obtained when separate samples were used at each temperature as was previously shown in figure 2. The results obtained by this method are compared in figure 5 (curve *A*) with the results obtained when separate samples were heated for 7 days at the specified temperature (curve *B*). The new method gives slightly higher results than the original because the samples remain heated for a longer period. At the highest temperature, the difference is, however, no greater than 2.5 percent, which appears to be sufficiently accurate. This method was therefore used in comparing the stabilities of the different vegetable-tanned leathers.

(a) RATES OF EVOLUTION OF CARBON DIOXIDE

The amounts of carbon dioxide evolved from single samples of chestnut, sumac, cutch, and quebracho leathers and hide powder on heating for 7 days at each successive temperature in the presence of oxygen are shown in figure 6. The amounts of carbon dioxide are expressed as percentages of the weight of tannin substance, including both tannin and nontannin. Since hide powder as shown in the

figure gives off comparatively small amounts of carbon dioxide, the source of this gas is apparently the tannin substance. Therefore, if the results are calculated on the basis of equal contents of tannin

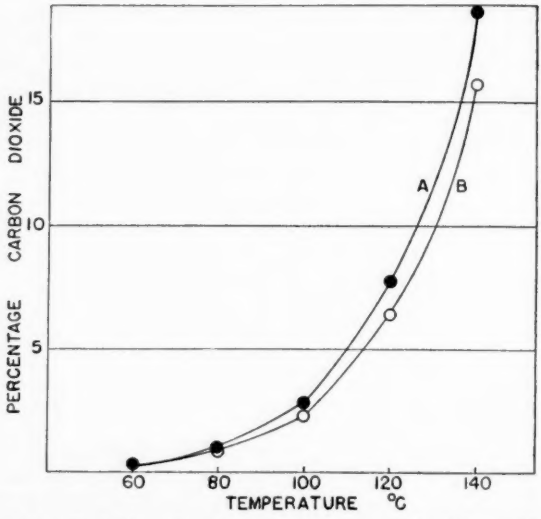

FIGURE 5.—*Evolution of carbon dioxide from chestnut-tanned leather.*

Curve *A*, single sample heated 35 days, 7 days at each constant temperature. Curve *B*, separate samples, each heated 7 days at constant temperature. Percentages based on the weight of the conditioned leather.

substance, a better basis for comparison is obtained. Chestnut leather gives off carbon dioxide at the highest rate and quebracho leather evolves this gas at the lowest rate. The order of decreasing rate of evolution of carbon dioxide by the leathers at every temperature studied is chestnut, sumac, cutch, and quebracho.

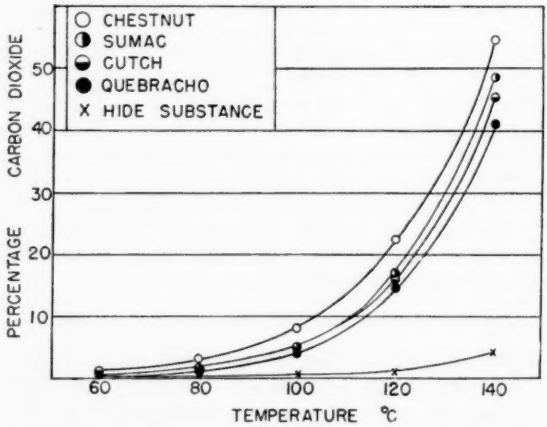

FIGURE 6.—*Effect of temperature upon the evolution of carbon dioxide from hide substance and from chestnut-, sumac-, cutch-, and quebracho-tanned leathers when heated in oxygen.*

Percentages for the leathers are based on the weight of tannin substance in the conditioned leathers. Percentages for hide substance are based on the weight of conditioned hide substance.

The comparative stabilities in the presence of oxygen, air, helium, or nitrogen with increase in temperature, as shown by the rates of evolution of carbon dioxide, are presented in figure 7, where average results for all the leathers are plotted. The results for each leather are given in table 1. The average results in the figure indicate that the increase in the amounts of carbon dioxide evolved for each 20-degree rise in temperature in either air or oxygen is in the majority of cases a multiple of approximately 3. The ratio of the amount given off in air to that evolved in oxygen is less than 1 to 3 and is therefore not proportional to the partial pressure of oxygen. The results for the individual leathers in the table indicate that in the case of chestnut leather the ratio of the amount of carbon dioxide evolved in air to that evolved in oxygen is almost exactly 1 to 2 for every temperature studied, while for the other leathers it is more nearly 1 to 3. Since only small amounts of carbon dioxide are produced in the presence of helium, it is evident that the reaction is an oxidation.

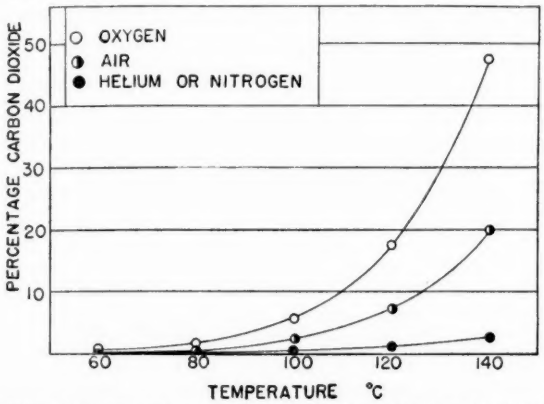

FIGURE 7.—*Effect of temperature upon the evolution of carbon dioxide from vegetable-tanned leathers heated in the presence of either oxygen, air, or one of the inert gases, helium or nitrogen.*

The experimental points represent averaged results from chestnut-, sumac-, cutch-, and quebracho-tanned leathers. Percentages are based on the weight of tannin substance in the conditioned leathers.

TABLE 1.—*Evolution of carbon dioxide from hide powder and vegetable-tanned leathers*

[Results for the leathers are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature—				
		60° C	80° C	100° C	120° C	140° C
		% CO_2	% CO_2	% CO_2	% CO_2	% CO_2
Chestnut	Oxygen	1.02	3.15	8.31	22.68	54.72
	Air	.47	1.52	4.26	11.28	27.61
	Helium	.26	.52	1.14	2.48	5.16
Sumac	Oxygen	.75	1.81	4.92	16.93	48.90
	Air	.20	.51	1.89	6.81	19.33
	Helium	.16	.20	.28	.75	2.95
Cutch	Oxygen	.60	1.43	4.94	16.26	45.66
	Air	.23	.54	1.94	6.20	18.17
	Helium	.09	.11	.23	.51	1.29
Quebracho	Oxygen	.43	1.19	4.17	14.50	41.20
	Air	.03	.30	1.25	4.55	14.74
	Nitrogen	.05	.08	.14	.41	1.06
Hide powder	Oxygen	.04	.10	.26	.95	4.05
	Air	.01	.02	.08	.32	1.21
	Nitrogen	0	0	0	.04	.18

(b) RATES OF EVOLUTION OF WATER

No attempt was made in this work to distinguish definitely between adsorbed water, water resulting from dehydration reactions, or water resulting from oxidation reactions. For purposes of comparison, all water evolved by heating at 60° C for 1 week may be considered as adsorbed water. For chestnut leather this value for adsorbed water at 60° C was 0.7 percent less than that obtained at 100° C by a method similar to the ALCA method for determining the moisture contents of leathers. The difference between the amounts of water given off at 60° C and that given off at a higher temperature was then considered as either water resulting from oxidation or dehydration reactions. These results for all the leathers, based on the content of tannin substance and for hide substance, are given in table 2. It may be observed that chestnut leather emits the least amount of water in the presence of air or oxygen, while, in general, cutch and quebracho evolve the most. The differences in the amounts emitted are, however, not large. Hide powder evolves much less water than any of the leathers.

TABLE 2.—*Evolution of water resulting from dehydration and oxidation reactions from hide powder and vegetable-tanned leathers* [1]

[Results for the leathers are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature—			
		80° C	100° C	120° C	140° C
		% H_2O	% H_2O	% H_2O	% H_2O
Chestnut	Oxygen	2.62	6.03	14.02	31.02
	Air	2.27	4.93	10.32	21.28
	Helium	2.45	3.59	5.57	9.27
Sumac	Oxygen	2.28	5.31	13.94	33.90
	Air	2.09	3.82	8.90	20.39
	Helium	1.38	2.09	4.72	8.03
Cutch	Oxygen	1.97	6.17	16.20	37.34
	Air	1.77	4.29	10.06	21.97
	Helium	1.03	1.80	3.37	6.57
Quebracho	Oxygen	2.30	6.29	15.28	32.17
	Air	1.14	3.12	8.02	17.94
	Nitrogen	.92	1.46	2.84	5.83
Hide powder	Oxygen	.38	.80	2.05	5.83
	Air	0	.24	.92	2.78
	Nitrogen	0	.13	.28	.99

[1] These results represent the differences between that evolved at the indicated temperature and that evolved at 60° C.

The amounts of water given off in oxygen or air and the amounts in helium or nitrogen with increase in temperature are compared in figure 8, where the average results for all the leathers are plotted. These results, showing the amounts emitted at different temperatures, are similar to those obtained with regard to change in rate of evolution of carbon dioxide with increase in temperature and to the relative effects of oxygen, air and helium. The amounts of water evolved in the presence of helium indicate that only a part of the water obtained in the presence of oxygen and air can result from oxidation reactions. If the amounts obtained in helium are subtracted from those obtained in oxygen and air, then the ratio of the formation of water of oxidation in oxygen to that in air is approximately 2 to 1 at the higher temperatures. These results obtained with each leather are shown in table 3.

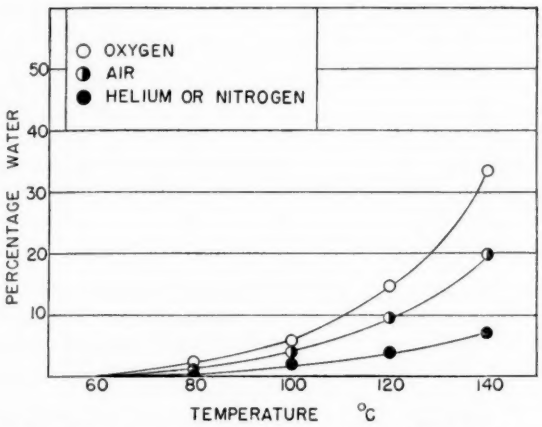

FIGURE 8.—*Effect of temperature upon the evolution of water from vegetable-tanned leathers heated in the presence of either oxygen, air, or one of the inert gases, helium or nitrogen.*

The experimental points represent averaged results from chestnut-, cutch-, sumac-, and quebracho-tanned leathers. Percentages are based on the weight of tannin substance in the conditioned leathers.

TABLE 3.—*Water resulting from oxidation reactions, evolved from vegetable-tanned leathers* [1]

[Results are based on the contents of tannin substance in the conditioned leather]

Leather	Gaseous atmosphere	Temperature			
		80° C	100° C	120° C	140° C
		% H_2O	% H_2O	% H_2O	% H_2O
Chestnut	Oxygen	0.17	2.44	8.45	21.75
	Air	−.18	1.34	4.75	12.01
Sumac	Oxygen	.90	3.22	9.22	25.87
	Air	.71	1.73	4.18	12.36
Cutch	Oxygen	.94	4.37	12.83	30.87
	Air	.74	2.49	6.69	15.40
Quebracho	Oxygen	1.38	4.83	12.44	26.32
	Air	.22	1.66	5.18	12.09

[1] These results represent the differences between that evolved in the presence of either air or oxygen and that evolved in the presence of helium or nitrogen at the same temperatures.

IV. GENERAL DISCUSSION

A relationship appears to exist between the type of tanning material and amounts of carbon dioxide and water evolved. Chestnut and sumac tannins are generally classified with the pyrogallol group of tannins, while quebracho and cutch are classified with the catechol tannins. The former give off more carbon dioxide in the presence of air and oxygen than the latter, which is in accordance with Jany's findings [1] that the amount of oxidation taking place depends in part upon the number of hydroxyl groups in the tannin molecule. Chestnut and sumac leathers heated in the presence of helium also give off more water and more carbon dioxide than the cutch and quebracho leathers heated under similar conditions. This is an indication that these tannins are of such a nature as to permit considerable direct break-down. Another point of similarity among the

members of each of the two classes of tannins is the fact that quebracho and cutch in general evolve more water resulting from oxidation reactions than chestnut and sumac.

No definite mechanism can be proposed for the breakdown of the tannins during the formation of carbon dioxide and water by oxidation. An interesting relation may be observed, however, from a study of the reaction products formed when a simple compound related to the tannins, such as pyrogallol, is oxidized [6] to purpurogallin, carbon dioxide, and water as follows:

$$4C_6H_6O_3+3O_2\longrightarrow 2C_{11}H_8O_5+2CO_2+4H_2O.$$

Thus in the course of this reaction 1 atom of carbon to 4 hydrogen are oxidized to carbon dioxide and water, respectively. From the results obtained in this work the ratio of carbon to hydrogen in the amounts of carbon dioxide and water evolved from chestnut and sumac tannins, which have the pyrogallol nucleus, is about 1 to 3.

The amount of water evolved does not appear to be directly related to the stabilities of the leathers; for example, chestnut leather is least stable with regard to the amounts of carbon dioxide evolved

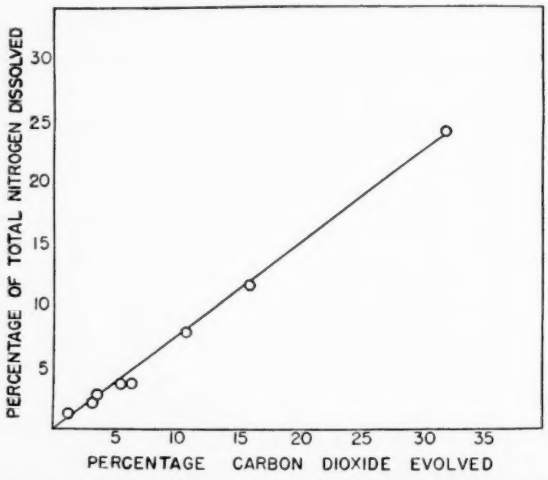

FIGURE 9.—*Correlation of the amounts of carbon dioxide evolved from vegetable-tanned leathers with the percentages of the total nitrogenous materials extractable by a 0.1 N solution of sodium carbonate.*

Percentages are based on the weight of the conditioned leather.

and to the amounts of nitrogenous materials extractable, but it gives off less water than any of the other leathers, while quebracho leather is most stable in these respects but gives off more water than chestnut leather. An explanation for this fact is apparent from a study of some of the reaction products probably formed in the course of the oxidation of a tannin. In the first stages of these oxidations quinones are formed. The formation of quinones by oxidation of polyphenols results in the elimination of water. Since quinones have strong tanning properties, the tanning effect of a polyphenol might actually be enhanced by oxidations in which water is formed.

The present work and the results from previous work indicate that the amounts of carbon dioxide evolved are related to the comparative stabilities of the leathers under various conditions. In a previous paper [5] the increase in the percentages of the total nitrogenous materials extractable from leathers with increase in the temperature of aging in the presence of either oxygen, air, or helium is shown. The curves in figure 4 of that paper are similar to those shown in figure 7 of the present paper, where the increases in the amounts of carbon dioxide evolved with temperature of heating are given. The results in these two figures were combined by plotting the percentages of the total nitrogenous materials extractable at one temperature, against the carbon dioxide evolved at the same temperature. This is shown in figure 9. A linear correlation is obtained between the carbon dioxide evolved and the percentages of the total nitrogenous materials extractable. It therefore appears that the chemical breakdown in the tannins is directly related to the chemical deterioration that takes place in the hide substance.

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TESTING AND PERFORMANCE OF VOLT BOXES

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ABSTRACT

The apparatus and method used in the precise measurement of the ratio of volt boxes at the National Bureau of Standards are described in detail. The method is applicable with rated voltage applied to the volt box and has an accuracy approaching one part in 100,000. The results of such measurements on a number of volt boxes under various conditions of humidity and temperature are given as a guide to their use and an index of their accuracy.

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I. INTRODUCTION

A volt box, more appropriately called a "resistance potential divider," is a device commonly used to extend the range of a potentiometer by a definite factor so as to permit of the precise measurement of direct voltages which exceed the limited range of the potentiometer. Any error in this factor will of course enter directly into the measurement of voltage, and in cases where the volt box is used in connection with the testing of wattmeters or watthourmeters, into the measurement of the commercially valuable quantities, electric power and energy.

A volt box consists of a number of resistors connected in series and provided with binding posts so that the unknown voltage to be

measured can be connected to the whole of the series circuit (or to some relatively large fraction thereof), while the potentiometer is connected to measure the potential drop between the terminals of a smaller part of the circuit thus energized. In the absence of electric leakage, the ratio of the unknown voltage to the potential drop measured by the potentiometer is evidently equal to the ratio of the resistance of the whole circuit to that of the portion connected to the potentiometer. An accurate determination of this ratio thus constitutes a test of the volt box.

It will be seen that such a test involves only the ratio of two resistances and not their absolute values. Consequently a test of a volt box does not necessarily involve any measurements of resistance in terms of the International Ohm, but only the much easier process of relative measurement. A further result of this fact is that certain types of variation which affect all parts of the circuit equally, such as changes in room temperature, tend to cancel their effects leaving only very small residual errors. Theoretically it would be desirable if all parts of the circuit were formed of wire of the same size, composition, and treatment. Practical difficulties in making adjustments may arise if the length of fine wire required for any of the low ranges becomes too short. Sometimes this difficulty can be met by using a short length of larger manganin wire at one end of the small fine-wire coil and making the final adjustment on this larger wire. Also, the construction of coils of very different resistance often produces differences in cooling surfaces and thus in load coefficient.

Volt boxes are, therefore, subject to a number of sources of error, two of which depend upon the applied voltage. First, the heat developed in the resistors when subjected to the operating voltage (sometimes as much as 1,500 volts) may create temperature differences and hence vary the relative resistance of the component parts. Second, any leakage over the insulating supports of the individual resistors will make the current in some of them differ from that in others, so that the ratio of voltages will not be the same as the ratio of resistances. It is evident that a design of volt box in which self-heating trouble has been made negligible by the use of a circuit of very high resistance will be particularly liable to leakage trouble, and vice versa. In view of the facts that in general the resistance of leakage paths does not obey Ohm's law, and that the resistance of manganin does not vary linearly with temperature, it is obviously very desirable that a volt box be tested under conditions as nearly as possible the same as those under which it is used, and in particular, that it be tested at operating voltages.

It is the purpose of this paper to describe the equipment used at the National Bureau of Standards for making such tests, and also to give typical data showing the performance of present commercial volt boxes, as a guide to other laboratories which may be called upon for similar testing work.

II. METHOD

The method of test here used is based on a comparison of the ratio of the volt box under test with that of a standard volt box of the same nominal range, the ratio of which has been determined by methods to be described. Of the various possible methods for making the intercomparison, the following has been found most flexible and convenient.

The two volt boxes are connected in parallel between junction points A and B, as shown in figure 1, and supplied with rated voltage, V. The corresponding terminals, such as S_3 and X_3 or S_2 and X_2, are then at very nearly equal potentials. If the small potential differences between these terminals are measured and denoted by v_1, v_2, v_3, and v_4, respectively, then the ratio, F_X, of the unknown is given by the equation

$$F_X = F_S\,(1+[(v_4-v_1)/V]-F_S\,[(v_3-v_2)/V]+\ \ldots\ .),$$

in which terms of the second and higher order in $F_S(v_3-v_2)/V$ and $(v_4-v_1)V$ have been neglected. Here any v is to be taken as positive if the X terminal is positive with respect to the S terminal when B

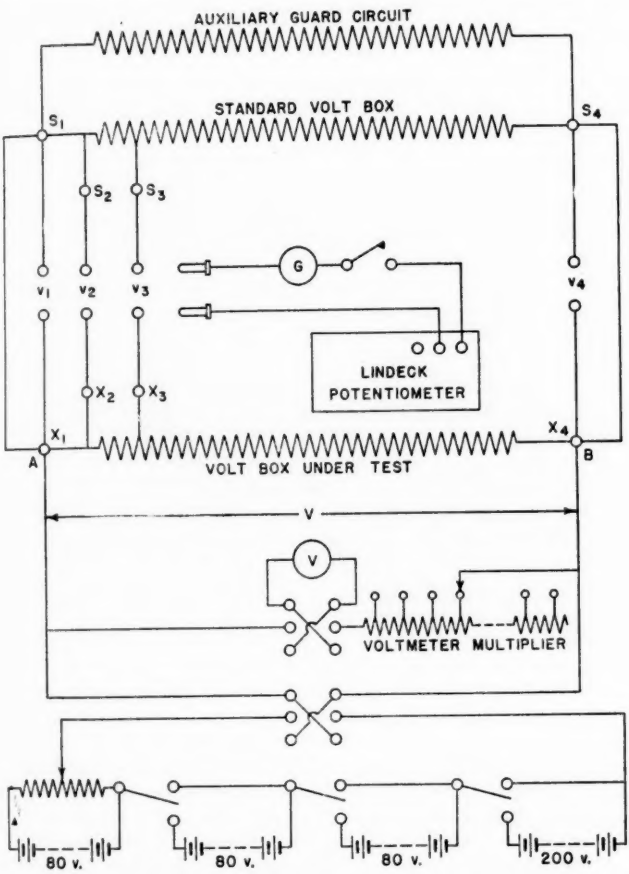

FIGURE 1.—*Diagram of circuit used to intercompare volt boxes by the first method.*

is positive with respect to A. The quantities v_4 and v_1 arise only from the resistance of leads and contacts and are always small (seldom more than 250 microvolts at rated voltage); v_2 is also usually small, and differs from v_1 only as the result of the resistance of connectors within the volt boxes. Furthermore v_3 is small (seldom exceeding

1,000 microvolts) unless the volt box under test is seriously out of adjustment. Consequently in measuring the small potential differences, v, and the applied voltage, V, only a moderate relative accuracy is sufficient to give a high precision in F_x. The applied voltage, V, is conveniently measured with a voltmeter, but the small potential differences, v, should be measured with a low-range potentiometer.

The three sections which follow describe in some detail the main components of the equipment used in this method at the National Bureau of Standards.

III. THE STANDARD VOLT BOX

The apparatus used at the National Bureau of Standards as a standard volt box is shown in figure 2, and its ranges are listed in column 8 of table 1 (p. 287). It was designed so as to minimize the two sources of error mentioned above and at the same time to provide for its own calibration in as simple a manner as possible. The self-heating error is kept low by the use of a high-resistance working circuit. This normally carries only 3 milliamperes (that is, its resistance corresponds to 333⅓ ohms per volt) so that at its rated 750 volts, the power dissipated is only 2.25 watts, which corresponds to 0.25 milliwatt per square centimeter of coil area. The total resistance is 250,000 ohms, and with a box of normal construction an error of 0.1 percent might be caused if the insulation resistance of the effective leakage path fell below 250 megohms. To reduce the error which could be caused by such leakage, the working circuit is divided into 11 parts no one of which has a resistance of more than 25,000 ohms. Nine of these parts consist of ten 2,500-ohm coils and the tenth of nine such coils. The coils of each part are carried by a panel of hard rubber. Each of these ten panels in turn is hung by metal blocks from the under side of the Bakelite top of the box, as shown in figure 3. The eleventh part consists of coils of lower resistance which are hung from a portion of the Bakelite top which is separated by a metal guard from the rest of the box. The hard-rubber panels for adjacent parts are spaced with a clearance of 5 mm, and any surface leakage from one panel to the next is intercepted by the supporting blocks. An auxiliary or "guard" circuit, corresponding sections of which can be connected in parallel with the working circuit, is provided with taps at appropriate points to which the metal supporting blocks are electrically connected. Each of the binding posts of the working circuit is also provided with a surrounding metal guard ring connected to a point on the guard circuit which has the same potential as that of the post. The result is that there can be no leakage paths which are normally subject to more than 75 volts or which shunt more than 25,000 ohms, and most of the insulation of the working circuit is subjected to only the very small differences of potential which result from lack of perfect adjustment of the guard circuit. The leakage errors on the high ranges are thus reduced by a factor of more than 100. The guard circuit has a nominal resistance of 266⅔ ohms per volt.

The calibration of the standard volt box requires the determination of the resistances of various parts of the working circuit relative to one another. The process consists in, first, the intercomparison of a group of sections of nominally equal resistance and then the connection

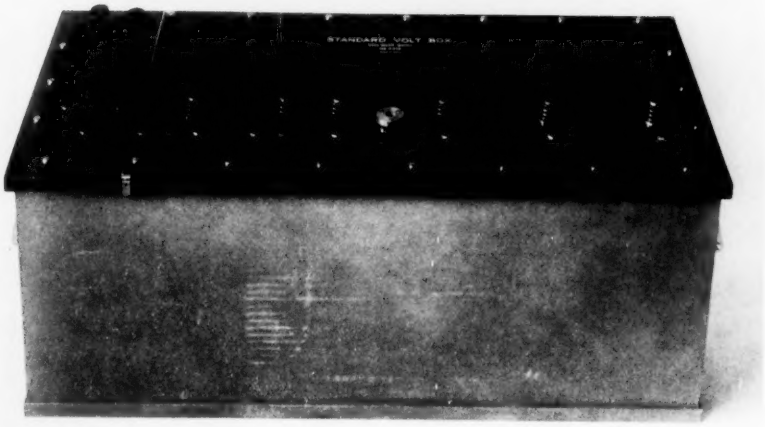

FIGURE 2.—*The standard volt box.*

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of these equal sections in series to form the first section of a group of larger denomination. If the resistance of the first section of a group of five is arbitrarily taken as a base, the first four intercomparisons give the separate resistances of the next four sections relative to this base. The addition of these values gives the resistance relative to the base of the entire group connected in series. This group itself constitutes the first section of the next group, the resistances of which are thus determined in terms of the original base. To minimize the number of individual sections while retaining the series of nominal ratios used in most commercial volt boxes, it was found desirable to use

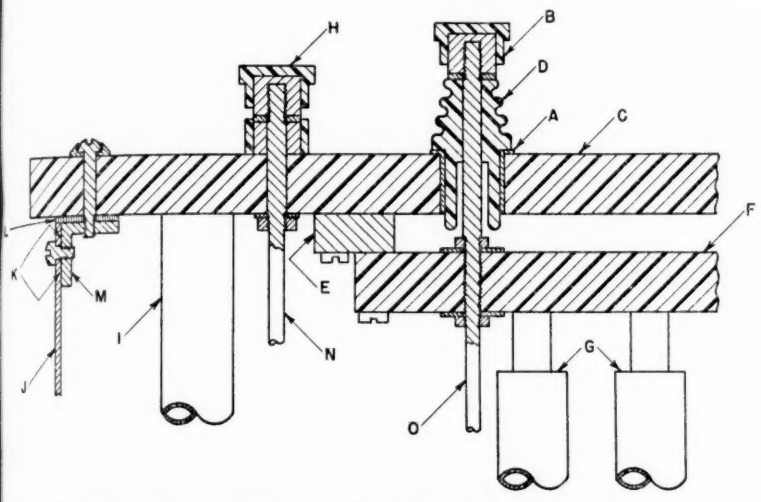

FIGURE 3.—*Cross section through a portion of the standard volt box.*

A, Metal guard ring connected to guard circuit.
B, A terminal of the standard volt box.
C, Bakelite top panel.
D, Insulator bushing.
E, Brass support for panel *F*. *E* is connected to the guard circuit.
F, Hard rubber panel.
G, Two resistance coils of the working circuit.
H, A guard-circuit terminal.
I, A resistance coil of the guard circuit.
J, Air-tight metal box.
K, Sweated air-tight joint.
L, Rubber gasket.
M, Metal angle.
N, Brass rod, which extends to bottom of *I*. A tap lead of guard circuit connects to bottom of *N*.
O, Brass rod extending to bottom of *G*. A tap from the working circuit connects to bottom of *O*.

groups containing alternately five and two nominally equal sections. Thus the first group consists of five sections of 50 ohms each which are rated at 150 millivolts each. These sections connected in series form the first 250-ohm section of the second group of two sections. These two 250-ohm sections in series form in turn the first 500-ohm section of the third group, which again consists of five sections. This scheme is carried along to the highest sections of 50,000 ohms each, which are rated for a potential drop of 150 volts.

The most convenient way of intercomparing the resistance of the sections of any one group is to substitute one after another in the unknown arm of a Wheatstone bridge as shown in figure 4 (*A* and *B*). This bridge circuit must be definite and sensitive to the full percentage accuracy desired in the volt-box calibration, but the corrections to its arms and the lead resistances ordinarily need not be known, provided they remain the same during the intercomparison of the sections of each group.

The intercomparison of the lower voltage sections by this substitution method can readily be made with full rated voltage applied to the section under test. To apply full voltage (150 volts) to the higher

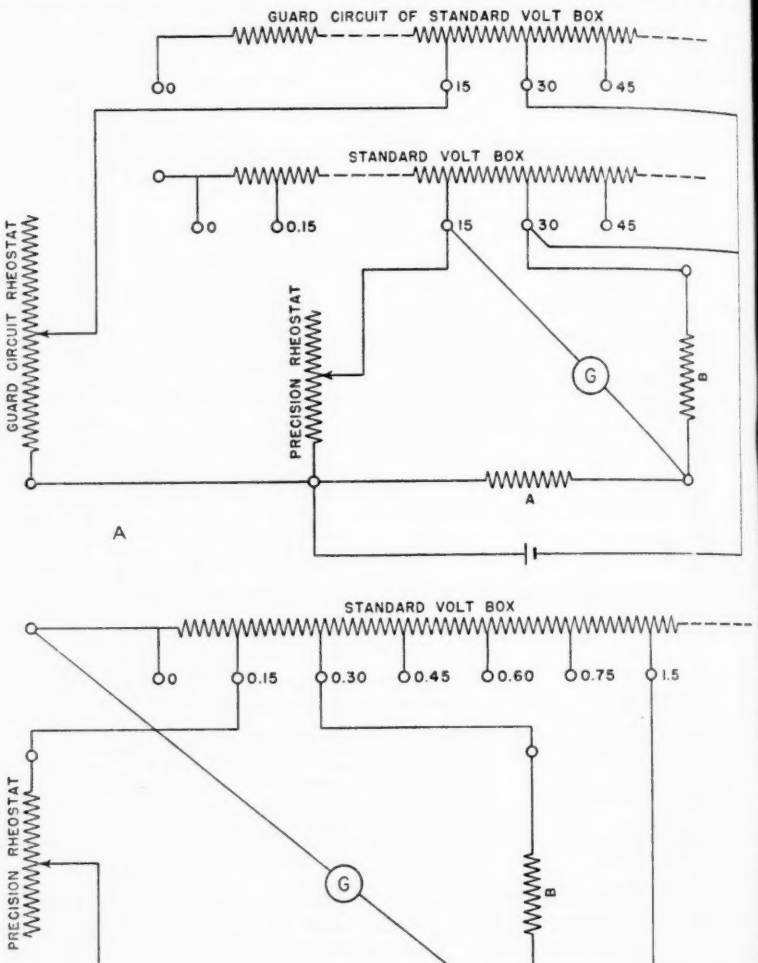

FIGURE 4.—*Bridge circuits for calibrating standard volt box.*

A, Higher sections. B, Lower sections.

voltage sections with the bridge arrangement of figure 4 (*A*) would require the use of a bridge arm of about 10,000 ohms, the resistance of which remains steady when dissipating 2.25 watts. Experiments

using such an improvised arm have shown that the ratio of the 50,000-ohm sections to the 500-ohm section is the same at 300 volts and at 150 volts as at 30 volts, within 3 parts per million. Routine calibrations are therefore made at only 30 volts. In the case of the high-voltage sections, the measurement should be made with the corresponding section of the guard circuit energized by connecting it to the battery which supplies the bridge current, as shown in figure 4 (*A*).

Table 1 (see p. 287) is the schedule used for computing the final volt-box corrections from the bridge readings. In the table each value of p is the observed resistance of the precision rheostat in the bridge circuit of figure 4 (*A* and *B*). The computed values of s in column 7 are the corrections in parts per million which, when applied to the nominal ratio of the resistance of the range in column 8 to the resistance of the 0 to 0.15 range, will give the actual ratio. To obtain the actual ratio for any range in column 8 to any other range listed in that column, subtract the value of s for the second range from that of the first and apply this difference as a correction in parts per million to the nominal ratio of the two ranges. The mathematical derivation of the equations of table 1 is given in appendix II.

The actual carrying out of a test by this procedure is very rapid, a complete test and computation for all ranges being obtainable in less than 3 hours. The sole theoretical error in the procedure as described arises from the resistance of the rods which lead from the junction points of the sections to the binding posts. The resistance of each rod is only 0.0006 ohm. If the rods are equal in resistance, the error will be equal to the resistance of two rods divided by the total resistance of the volt-box range used. Differences in rod resistance will cause errors equal to these differences divided by the resistance of the section measured. To eliminate this latter error in the measurements of the 50-ohm sections, the galvanometer and battery connections of the bridge circuit are made through the sections next adjacent to the one under test, as shown in figure 4 (*B*), and thus the rods are put into arms of higher resistance. The effect of the rod resistance on the volt-box ratio is less than 3 parts per million.

As a measure of the precision readily attainable in this process of calibration, data obtained over a period of 12 years were examined and 27 successive independent determinations of the ratio of two sections of identical construction, namely that between the 450- and 600-volt taps and that between the 600- and 750-volt taps, were tabulated. The standard deviation of these values from their mean was found to be 7 parts per million, the greatest individual deviation being 19 parts per million. This deviation, of course, includes any drift in the relative values of the coils involved as well as the errors in the setting up of their ratio.

The individual coils are wound with a single layer of silk-covered manganin wire, all coils being wound with wire from the same spool so as to minimize differences in the temperature coefficient of resistance of the various parts. Nevertheless, early data showed a tendency to a cyclical annual fluctuation in the ratio of the 750-volt to the 1.5-volt section amounting to about 30 parts per million. This is apparently the result of changing atmospheric humidity. To minimize such effects, a small air pump is arranged to maintain the average pressure within the standard volt box at 15 mm of water above atmospheric. Air from the pump passes through a drying vessel containing $CaCl_2$

and is thus thoroughly dried before entering the box. A rubber gasket between the metal box and the Bakelite top seals the joint sufficiently so that an air flow of about 0.1 m^3 per 24 hours is enough to maintain the pressure differential. Since the installation of this dry-air supply, the cyclic fluctuation has been very small.

IV. THE LINDECK POTENTIOMETER

The potentiometer generally used for measuring the small voltages, v_1, v_2, v_3, and v_4, referred to in section II is of the Lindeck type.[1] Figure 5 is the circuit diagram of this instrument. In this device a current

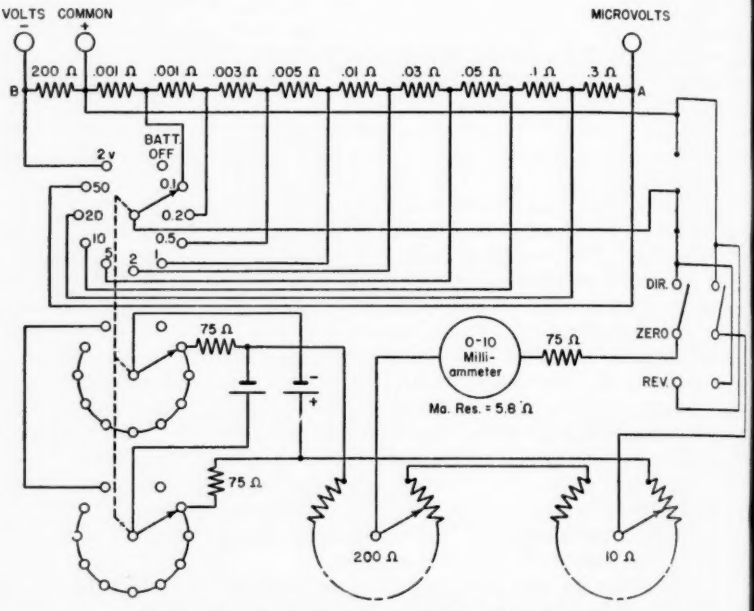

FIGURE 5.—*Circuit of the Lindeck potentiometer.*

When intercomparing volt boxes, the terminals labeled "common" and "microvolts" are used. When interchecking the calibrations of the potentiometer and the voltmeter, the terminals labelled "common" and "volts" are used.

measured by the milliammeter passes through a selected portion of the standard resistor, AB, and this current is adjusted until the voltage drop in the standard resistor is exactly equal and opposite to the voltage to be measured, as indicated by the external galvanometer (shown at G in fig. 1), which is used as a null indicator.

The milliammeter has a scale length of approximately 15 cm and is equipped with a parallax mirror. It requires 10 ma for full-scale deflection.

The standard resistance sections between A–B in figure 5 are made of manganin and are so constructed that the temperature rise is negligible even with the current of 8 amperes which is used to calibrate them on a Kelvin double bridge. Their resistance should be adjusted

[1] J. C. Poggendorff, Ann. Phys. Chem. **54**, 161 (1841); Lindeck and Rothe, Z. Instrumentenk. **20**, 23 (1900); H. B. Brooks and A. W. Spinks, BS J. Research **9**, 781 (1932) RP506. This last paper contains a brief summary of the two references above and a discussion of basic potentiometer circuits.

to a precision somewhat better than that to which the milliammeter can be read.

Since the resistance of the galvanometer circuit may vary from a low value for measurements of v_1, v_2, and v_4 up to several hundred ohms in the measurement of v_3, the time required to obtain a reading can be shortened by providing manganin rheostats in series and in parallel with the galvanometer, so that the instrument can be critically damped in all four measurements. In operation, the voltage applied to the volt boxes, and the potentiometer current are reversed simultaneously, so that the effect of any constant thermal emf in the galvanometer circuit or elsewhere is eliminated. By moderate care in using only copper and materials, such as manganin, which have a low thermal emf against copper, the residual emf is so small that fluctuations in it cause only negligible errors.

The external galvanometer has a sensitivity of 3 mm per microvolt at 1 m distance, with a critical external damping resistance of 200 ohms and a period of 5.8 seconds.

V. AUXILIARY FEATURES

All of the wires in the measuring circuits are run in shielded cable, and each shield is maintained at the same potential as the wire inside it by means of the auxiliary "guard" circuit of the standard volt box mentioned in section III above. The galvanometer and the Lindeck potentiometer are mounted on metal guard plates which are so located as to intercept any possible leakage currents. When voltage v_1, v_2, or v_3 is being measured, these guard plates are connected to the low-voltage terminal of the auxiliary guard circuit of the standard volt box; but when v_4 is measured, these plates are connected to the high-voltage terminal of the guard circuit. A special plug-connector panel is used to connect the Lindeck potentiometer circuit to measure v_1, v_2, v_3, and v_4, and this panel is designed so that guard plates intercept leakage currents between the different measuring circuits.

For test voltages from 400 to 750 volts the batteries shown in figure 1 are replaced by a motor-driven d-c generator. The driving motor and the field of the generator are energized by means of batteries.

With this equipment, 750 volts is the nominal limit at which volt boxes are tested. However, experiment has shown that the calibration of the standard volt-box can be relied upon up to 1,500 volts, and by special arrangements the generator can be connected in series with a group of batteries to obtain this voltage.

Since this method of calibrating a volt box involves the ratio of the small voltages measured by the potentiometer to the larger voltage measured by the voltmeter, it is necessary that the readings of these two instruments be mutually consistent, though neither need be accurate. Means were therefore provided for readily intercomparing them. This is done by applying the same voltage to the voltmeter and the standard volt box and measuring the voltage drop across the 0 to 1.5-volt range of the standard volt box with the Lindeck potentiometer. The "volts" and "common" terminals (see fig. 5) of the potentiometer are used. Knowing the volt-box ratio, the agreement of the two instruments can be readily checked. Since the volt-

meter is provided with a shunt circuit around the moving element to provide temperature compensation in the manner described by Brooks,[2] it was found convenient to incorporate in this shunt circuit a small rheostat which can be used to adjust the current through the moving element, so that the calibration of the voltmeter may be made consistent with that of the potentiometer in spite of any small changes in either instrument.

VI. TEST PROCEDURE

When a volt box is received for test at the National Bureau of Standards, the resistances between its terminals are first measured with a Wheatstone bridge, in order to detect any defective resistance coils before full voltage is applied to them. Data from these measurements can also be used to compute the approximate ratio. The volt box is then connected into the circuit of figure 1, and voltage is applied. Voltages v_1, v_2, v_3, and v_4 are then measured successively, by adjusting the Lindeck potentiometer until the simultaneous reversal of polarity of the applied voltage, V, and of the potentiometer does not change the galvanometer deflection. This latter procedure makes negligible those errors that might be caused by any constant thermal emf in the galvanometer circuit. Because of the self-heating effect, to be described in section VII–5, the volt box is then allowed to warm up until the measured value of v_3 becomes reasonably constant. If the volt box has more than one range, the highest range is measured first and then the other ranges are measured in order of decreasing ratio. This procedure requires only one warming-up period for the entire box.

A very effective check on the accuracy of the measurements is obtained by making two independent measurements of each ratio of the volt box under test, using two different standard volt-box connections which give the same ratio. Examples of standard volt-box terminal arrangements which give the same ratio are: 0–1.5–150, 0–3–300, 0–6–600, and 0–7.5–750.

Ratios of the tested volt box are computed by means of the equation given in section II. If for any range the total change in ratio caused by self-heating is greater than the precision (0.01 percent) to which results are reported, then the observed change and the time required to complete it are reported.

VII. TYPICAL PERFORMANCE CHARACTERISTICS OF VOLT BOXES

Although the technical literature abounds with articles on potentiometers and much has been done to improve their accuracy, volt boxes are mentioned only incidentally and with the exception of manufacturer's guarantees, no literature appears to have been published which discusses the factors affecting the accuracy of the voltage ratio of volt boxes. Perhaps the reason for this lack of published information is that up to the present time the accuracy of the measurements in which volt boxes have been used has not been noticeably limited by any variation in the voltage ratio of the latter. In view of this situation, a somewhat detailed discussion is given below of the

[2] H. B. Brooks, J. Research NBS **17**, 523 (1936) RP926.

factors which affect the voltage ratio so that those who use volt boxes may know what factors may affect measurements of a given precision.

At the time of the construction of a volt box the departure of its actual voltage ratio from the nominal value will depend upon the care with which the manufacturer adjusts the resistances of the various coils. Thereafter the departure of the voltage ratio from the intial value may depend upon (a) secular change of the resistance of the coils, (b) ambient temperature, (c) temperature changes caused by self-heating, (d) slow seasonal variations in ratio caused by seasonal changes in relative humidity, and (e) changes in insulation resistance between terminals and between the coil studs.

1. ACCURACY OF MANUFACTURER'S ADJUSTMENT OF RATIO

Figure 6 indicates the accuracy of the manufacturer's adjustment of voltage ratio on 86 volt boxes tested at the National Bureau of

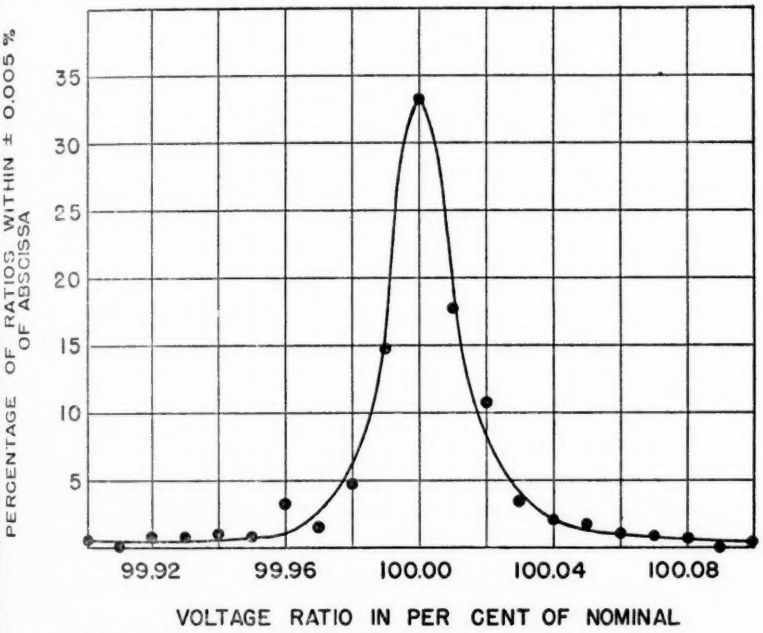

FIGURE 6.—*Accuracy of the manufacturer's adjustment of voltage ratio.*

This curve represents data on 86 volt boxes tested at the National Bureau of Standards between 1927 and 1940. In computing the curve each range of a multiple-range volt box was considered separately, so that there were 413 ranges tested.

Standards between the years 1927 and 1940. For each plotted point in this figure the ordinate represents the percentage of volt-box ranges tested the ratio of which was within ±0.005 percent of the ratio indicated by the abscissa. If the volt box was tested on more than one occasion, only the results of the initial test were used in locating this curve. Curves of this type for individual ranges had the same

general shape and distribution of points as the composite curve shown here. All of the volt boxes represented in this curve were for 1.5-volt potentiometers. However, a curve of this type based on tests of a small number of volt boxes used with 150-millivolt deflection potentiometers displayed a similar shape and distribution of points.

2. SECULAR CHANGE

One would expect that the secular change of ratio would be less than the secular change of resistance of the individual coils, provided that all of the coils are of similar construction. Data are available on seven volt boxes which have been sent in to the National Bureau of Standards for annual test over periods of from 6 to 10 years. Of these seven volt boxes, the voltage ratio of the 150-volt to the 1.5-volt range has varied 0.01 percent, or less, in six of them, and the ratio of the seventh has increased uniformly by a total of 0.04 percent in a 10-year period. The other ranges of each volt box in this group varied in the same manner as the 150-volt to the 1.5-volt range. It may be supposed that this performance is typical of high-grade volt boxes.

3. SEASONAL VARIATION OF RATIO

It has long been known that resistance coils of silk-covered manganin wire, such as those used in many volt boxes, are subject to seasonal variations in resistance which are primarily due to seasonal variations in relative humidity. In 1936 Dike [3] published the results of his investigation of the phenomenon. He found that the silk threads

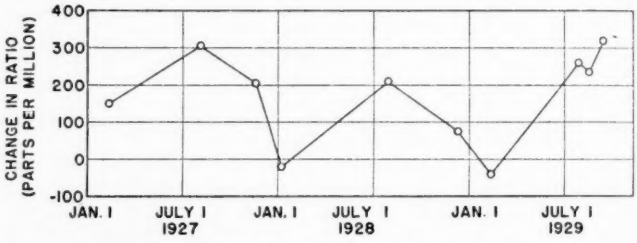

FIGURE 7.—*Seasonal variation of ratio for volt box A.*

Construction features of *A* are described under figure 8.

used to insulate the manganin wire had a greater length at high relative humidity than at low, and he concluded that this property of the silk was responsible for the fact that the resistance of silk-insulated manganin wire coils is greater at the higher humidities. He also found that if such coils were coated with certain waxes and suddenly changed from an atmosphere of one relative humidity to that of another, the resistance change would require approximately 3 weeks to complete, but that coils not coated with wax required less than 24 hours although the magnitude of the change in resistance was the same. The percentage change of resistance is greater the finer the wire.

Figure 7 shows the seasonal variation in ratio for a volt box in which the wire size is much larger on the low-voltage coil than on the coils nearer the high-voltage end. Dike's theory explains this curve very well, because from that theory we would expect the humid summer

[3] P. H. Dike, Rev. Sci. Instr. **7**, 278 (1936).

air to produce a greater percentage increase in the resistance of the fine wire coils than in the coarser wire of the low-voltage coil and hence make the voltage ratio higher during the summer months than in the drier winter months. It should be noted that artificial heating in winter causes the relative humidity indoors to be materially lower than that of the outside air. This curve should not be interpreted

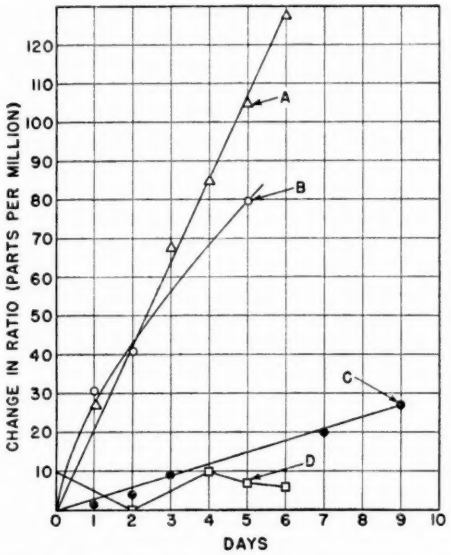

FIGURE 8.—*Drift of voltage ratio after a sudden increase in relative humidity.*

Each volt box stood for several weeks in a room having a relative humidity between 25 and 40 percent, and was then placed in a closed cabinet in which a saturated solution of sodium chloride maintained a relative humidity of 75 percent. Each curve represents measurements made on the 150-volt to the 1.5-volt range of a volt box, with the exception of the curve for volt box *A* on which the 150-volt to the 0.15-volt range was measured.

Volt box *A* has a resistance of 40 ohms per volt, its wood spools are wound with silk-insulated wire, and the diameter of the wire on the low-voltage coils is approximately 10 times that of the wire on the high-voltage coils.

Volt box *B* has a resistance of 200 ohms per volt, its metal spools are wound with silk-covered wire, and the ratio of the diameter of the wire in the low-voltage coil to that of the wire in the high-voltage coil is intermediate between that of volt boxes *A* and *C*.

Volt box *C* has a resistance of 26⅔ ohms per volt, its wood spools are wound with silk-covered wire, and the diameter of the wire in the low-voltage coil is twice that of the wire in the high-voltage coils.

Volt box *D* has a resistance of 333 ohms per volt; its metal spools are wound with enameled wire which is insulated with a patented mixture of silk and cotton, and the ratio of the diameter of the wire in the low-voltage coils to that of the wire in the high-voltage coils is approximately the same as that of *C*.

The coils of all four volt boxes are wax-coated.

as a typical curve for all volt boxes, since it probably represents an extreme type of construction among volt boxes built by reputable manufacturers.

To obtain additional data on the effects of humidity, an air-tight cabinet was built in which a volt box could be placed. A tray of saturated sodium chloride solution kept the relative humidity constant at 75 percent. Shielded leads were brought out so that the ratio of the volt box could be measured without opening the cabinet. Data for each of the curves in figure 8 were obtained by placing in this cabinet a volt box which for several weeks previously had been in an atmosphere having a relative humidity of less than 40 percent, and then periodically measuring the voltage ratio without removing

the volt box from the cabinet. These ratio measurements were made on the 150-volt range of each volt box with only 30 volts applied so as to make any self-heating effects negligible.

Volt boxes *A*, *B*, and *C* have coils wound with silk-covered manganin wire. The manganin wire of volt box *D*, however, is insulated with a patented [4] combination of silk and cotton, which is claimed to cause much less seasonal variation of resistance with humidity. The improvement is obvious from the curves.

These curves for volt boxes in which silk-covered manganin is used bear out two implications from Dike's paper. First, for a given voltage ratio the effect of a change in humidity will be least for the volt box having the fewest ohms per volt, since such a box will usually have thicker wire; this would explain the small effect on the ratio of *C* in figure 8. Second, the greater the difference between the wire diameters of the low-voltage and high-voltage coils, the greater will be the effect of humidity. This is shown by the curves for *A* and *B*, where *A* has one-fifth of the ohms per volt of *B* but the greater difference in wire size.

After the data for figure 8 were obtained, volt box *A* was kept in the cabinet for 4 weeks, and its ratio was found to have increased 0.048 percent in that time. Upon removing it from the cabinet to the dry air of the room, the ratio decreased exponentially, with a change of 0.029 percent the first week. Although the experiments reported above were made on a limited number of volt boxes, the results probably indicate the magnitude and character of the effects that would be experienced in the actual use of volt boxes.

4. EFFECT OF SURFACE RESISTANCE OF INSULATING PANEL ON THE RATIO OF VOLT BOXES

Some of the coil studs and binding post terminals of volt box *C*, which had the customary hard-rubber top, were disconnected from the coils and the insulation resistance between them was measured. Computations based on these measurements showed that surface leakage between coil studs and between terminals of a volt box would cause variations in the ratio of less than 5 parts per million for a relative humidity of 75 percent or less, provided the resistance was less than 400 ohms per volt, terminal spacings were 1¼ inch or more for 150 volts, and the coil stud spacings were 1 inch or more.

However, it is probable that at some relative humidity higher than 75 percent the surface resistivity of the panel of a volt box would become low enough to have a serious effect on the ratio.

5. EFFECT OF SELF-HEATING

For most of the volt boxes tested at the National Bureau of Standards during the past 13 years, it has been found that the ratio decreases during the first hour or two that rated voltage is applied, and remains nearly constant thereafter until the voltage is removed. The decrease is an exponential one, and the magnitude of the change for the 300-volt range in volt boxes having a resistance of 200 ohms per volt has been found to range from 0.005 percent to 0.03 percent, the average value being about 0.02 percent. One-half of this change occurs in about 20 minutes for most volt boxes.

[4] P. H. Dike. U. S. Patent 2,026,616, issued Jan. 7, 1936.

Two volt boxes having a resistance of 333 ohms per volt and a maximum resistance per coil of 5,000 ohms were found to show no measurable change in ratio even after several hours at rated voltage. The 750-volt range of a volt box having 100 ohms per volt showed a change in ratio of 0.04 percent in 2 hours at rated voltage.

Two factors are responsible for this self-heating effect. First, the resistance wire has an appreciable temperature coefficient of resistance; and second, for reasons of economy in construction the resistance coils in the higher voltage sections are usually on spools of approximately the same physical dimensions as those between the potentiometer taps, but have a much greater resistance per spool and hence a much greater temperature rise. The grade of manganin usually used in volt boxes has its maximum resistance near room temperature, and hence, as the higher resistance coils heat up, their resistance becomes a smaller percentage of the cold value than does that of the coils between the potentiometer taps. Hence, the voltage ratio of the volt box decreases.

Thermocouples were attached to the coils of a volt box of the usual construction having 200 ohms per volt. It was found that for the 9,000- and 10,000-ohm coils the temperature rise was 10° C as compared with 4° C for the 300-ohm coil. The ratio decreased with time on a smooth exponential curve for both the 150-volt range and the 300-volt range, the total change being 0.005 percent.

For volt boxes of normal construction the temperature rise of the coils is negligible at 20 percent of rated voltage, so that if the ratio of a volt box at rated voltage differs from that at 20-percent voltage by an amount that is negligible for a given measurement then the heating effect will also be negligible for that measurement.

VIII. APPENDIX I

Alternative Test Method

A method which is simpler than that described in section II and which is for many purposes amply accurate for comparing the ratio F_X, of an unknown volt box with that, F_S, of a standard volt box is shown in figure 9. Here H_X and P_X are the resistances of the high-voltage side between b and 4 and of the potentiometer side between a and b, respectively, of the box under test, and H_S and P_S are the corresponding resistances of the standard. Hence, by definition (provided the resistances of the connections from 1 to a and from 1′ to d are negligible in comparison with H_X+P_X and H_S+P_S, respectively),

$$F_X=\frac{H_X+P_X}{P_X} \text{ and } F_S=\frac{H_S+P_S}{P_X}.$$

The galvanometer is first connected between the terminals 2 and 2′ and the slider between 1 and 1′ is adjusted to give a balance. This assures that the resistances of the two sides of the rheostat, together with the leads to a and to d, are in the ratio

$$\frac{L_X}{L_S}=\frac{P_X+H_X+R_X}{P_S+H_S+R_S}=\frac{i_S}{i_X}.$$

The galvanometer is then shifted to join 3 and 3′, and one of the auxiliary resistors R_S or R_X as needed is increased until a balance is again reached. This gives the relation

$$\frac{L_X+P_X}{L_S+P_S}=\frac{H_X+R_X}{H_S+R_S}=\frac{i_S'}{i_X'}.$$

When by successive adjustment a balance is obtained for both positions of the galvanometer

$$\frac{i_x}{i_s}=\frac{i_x'}{i_s'},$$

so that

$$\frac{P_x}{P_s}=\frac{H_x+P_x+R_x}{H_s+P_s+R_s}.$$

Whence

$$F_x=F_s\left[\frac{\left(1+\frac{R_s}{H_s+P_s}\right)}{\left(1+\frac{R_x}{H_x+P_x}\right)}\right].$$

In actual practice R_x or R_s is left zero according as F_x is greater or less than F_s, so that the formula becomes very simple. This procedure does not fully eliminate the effect of the connections between points 1 and a and between 1′ and d, but such

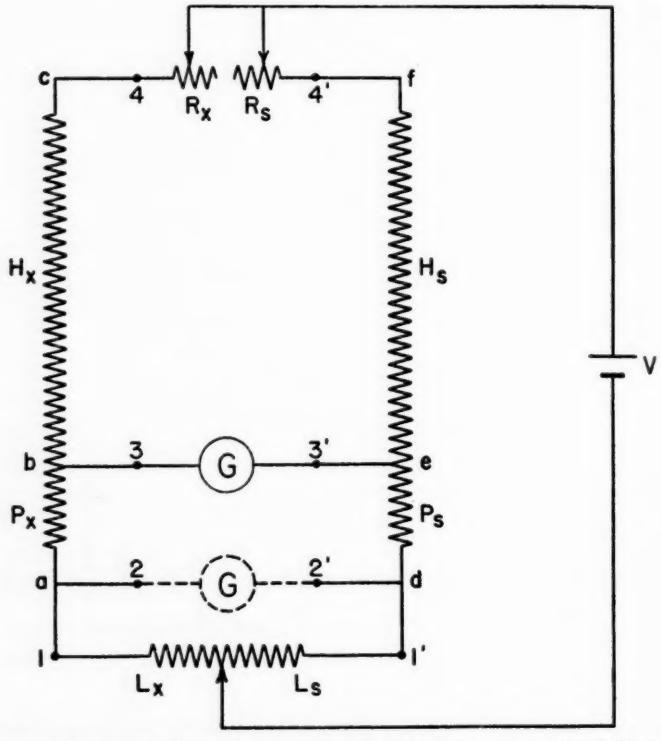

FIGURE 9.—*Schematic diagram of circuit for intercomparison of volt boxes by the alternative method.*

lead resistances are usually quite negligible. It also requires the measurement, though with only very moderate precision, of H_S+P_S (or H_X+P_X). For boxes of different resistances a wide range of values of R_X (or R_S) is required.

IX. APPENDIX II

Derivation of Test Schedule for Calibrating the Standard Volt Box

The working circuit of the standard volt box can be considered as made up of a succession of groups each made up of a number of sections. The first five sections of any one group have nominally equal resistances, and the last section has a resistance nominally five times this value. The first (counting from the low-potential end) section of each group is formed by all the preceding groups connected in series. Any section therefore can be identified by specifying two integers, the first, m, indicating the group of which the section is part, and the second, k, indicating the position of the section in its group.

If the Wheatstone bridge used in the successive measurements of the first five sections of the mth group has the fixed ratio B_m/A_m, then the resistance of the kth section is given by

$$R_{m,k}=\frac{B_m}{A_m}p_{m,k}, \tag{1}$$

where $p_{m,k}$ is the resistance of the rheostat arm when measuring section (m, k). Hence

$$R_{m,k}=R_{m,1}+\frac{B_m}{A_m}(p_{m,k}-p_{m,1})=R_{m,1}+\frac{B_m}{A_m}(n_{m,k}), \tag{2}$$

where $n_{m,k}$ is defined as $p_{m,k}-p_{m,1}$. The total resistance of the first five sections of the group is given by

$$\sum_{k=1}^{k=5}(R_{m,k})=5\,R_{m,1}+\frac{B_m}{A_m}\sum_{k=1}^{k=5}(n_{m,k}). \tag{3}$$

The bridge ratio is now changed to A'_m/B'_m and the bridge is balanced first across the combination of the first five sections in series giving

$$\sum_{k=1}^{k=5}(R_{m,k})=\frac{B_m'}{A_m'}p_{m,5} \tag{4}$$

and then across the sixth section giving

$$R_{m,6}=\frac{B_m'}{A_m'}p_{m,6}. \tag{5}$$

Hence

$$R_{m,6}-\sum_{k=1}^{k=5}(R_{m,k})=\frac{B_m'}{A_m'}(p_{m,6}-p_{m,5}). \tag{6}$$

We may write $p_{m,6}-p_{m,5}=n_{m,6}$ and combine eq 6 with eq 3 to get

$$R_{m,6}=5\,R_{m,1}+\frac{B_m}{A_m}\sum_{k=1}^{k=5}n_{m,k}+\frac{B_m'}{A_m'}n_{m,6}. \tag{7}$$

The resistance of the entire mth group is therefore

$$\sum_{k=1}^{k=5}R_{m,k}+R_{m,6}=10\,R_{m,1}+2\,\frac{B_m}{A_m}\sum_{k=1}^{k=5}n_{m,k}+\frac{B_m'}{A_m'}n_{m,6}. \tag{8}$$

A very convenient choice of bridge ratios, which keeps p nominally at 5,000 or 2,500 ohms, is to make

$$\frac{B_m}{A_m}=10^{m-3}\text{ and }\frac{B_m'}{A_m'}=10^{m-2} \tag{9}$$

Also, as an abbreviation, we may write

$$q_{m,5}=\sum_{k=1}^{k=5}n_{m,k}.$$

Inserting these values and noting that this total resistance of the mth group is identical with the resistance of the first section of the $(m+1)$th group we get

$$R_{(m+1,1)}=10\,R_{m,1}+2\times10^{m-3}q_{m,5}+10^{m-2}n_{m,t} \tag{10}$$

as the equation connecting resistance values in successive groups.

If this relation is applied successively, beginning with the first group ($m=1$), we get for the resistance of the first section of the mth group in terms of the resistance of the first section of the first group and the observed differences

$$\begin{aligned}R_{m,1}=10^{m-1}\,R_{1,1}&+10^{m-3}\,n_{m-1,t}+2\cdot10^{m-4}q_{m-1,5}\\&+10^{m-4+1}\,n_{m-2,t}+2\cdot10^{m-5+1}q_{m-2,5}\\&+10^{m-5+2}\,n_{m-3,t}+2\cdot10^{m-6+2}q_{m-3,5}\end{aligned}$$

Simplifying this we get

$$\begin{aligned}R_{m,1}&=10^{m-1}\,R_{1,1}+2\cdot10^{m-4}\,(q_{1,5}+q_{2,5}\cdots q_{m-1,5})\\&+10^{m-3}(n_{1,t}+n_{2,t}+\cdots\cdots n_{m-1,t}).\end{aligned} \tag{11}$$

The total resistance $S_{m,k}$ up to the kth tap in the mth group is derived from eq 2

$$S_{m,k}=\sum_{k'=1}^{k'=k}R_{m,k'}=k\,R_{m,1}+\frac{B_m}{A_m}\sum_{k'=1}^{k'=k}n_{m,k'} \tag{12}$$

Defining $q_{m,k}$ as $\sum_{k'=1}^{k'=k}n_{m,k'}$ and inserting the values of ratio from eq 9, we get

$$S_{m,k}=kR_{m,1}+10^{m-3}q_{m,k} \tag{13}$$

or by eq 11

$$\begin{aligned}S_{m,k}&=k\cdot10^{m-1}R_{1,1}+2\cdot10^{m-4}k(q_{1,5}+q_{2,5}\cdots q_{m-1,5})\\&+10^{m-3}k\left(n_{1,t}+n_{2,t}\cdots n_{m-1,t}+\frac{q_{m,k}}{k}\right)\end{aligned} \tag{14}$$

If the circuit is used as a volt box with the first section as the low-voltage side and the total resistance to the kth tap of the mth group as the high side, the actual ratio is $S_{m,k}/R_{1,1}$ and the nominal value is $k\cdot10^{m-1}$. The difference between these two values expressed in parts per million is, from eq 14

$$\begin{aligned}s_{m,k}=\frac{10^6}{k\cdot10^{m-1}}\left(\frac{S_{m,k}}{R_{1,1}}-k\cdot10^{m-1}\right)&=\frac{2{,}000}{R_{1,1}}(q_{1,5}+q_{2,5}\cdots q_{m-1,5})\\&+\frac{10{,}000}{R_{1,1}}\left(n_{1,t}+n_{2,5}\cdots\cdots n_{m-1,t}+\frac{q_{m,k}}{k}\right).\end{aligned} \tag{15}$$

The nominal value of $R_{1,1}$ is 50 ohms, so that

$$s_{m,k}=40(q_{1,5}+q_{2,5}\cdots q_{m-1,5})+200(n_{1,t}+n_{2,t}\cdots n_{m-1,t})+\frac{200}{k}\,q_{m,k}. \tag{16}$$

When the standard volt box is calibrated, it is usually desirable to obtain the corrections for all the taps in a single process. For this purpose the schedule of computation indicated in table 1 has been derived by, in effect, applying eq 16 to consecutively increasing values of k and of m. The quantities designated as $r_{m,k}$ constitute the last term in eq 16, and the summations indicated by the earlier terms are automatically made by the successive steps in computation.

TABLE 1.—*Schedule for computing corrections for the standard volt box*

Section in bridge arm	Bridge ratio *	Adjustable arm	n's	q's	r's	Correction	Range
1	2	3	4	5	6	7	8
0–0.15	100/10,000	$p_{1,1}$	$n_{1,1}=p_{1,1}-p_{1,1}=0$			$s_{1,1}=0$	0–0.15
0.15–0.30		$p_{1,2}$	$n_{1,2}=p_{1,2}-p_{1,1}$	$q_{1,2}=n_{1,2}$	$r_{1,2}=100q_{1,2}$	$s_{1,2}=r_{1,2}$	0–0.30
0.30–0.45		$p_{1,3}$	$n_{1,3}=p_{1,3}-p_{1,1}$	$q_{1,3}=q_{1,2}+n_{1,3}$	$r_{1,3}=67q_{1,3}$	$s_{1,3}=r_{1,3}$	0–0.45
0.45–0.60		$p_{1,4}$	$n_{1,4}=p_{1,4}-p_{1,1}$	$q_{1,4}=q_{1,3}+n_{1,4}$	$r_{1,4}=50q_{1,4}$	$s_{1,4}=r_{1,4}$	0–0.60
0.60–0.75		$p_{1,5}$	$n_{1,5}=p_{1,5}-p_{1,1}$	$q_{1,5}=q_{1,4}+n_{1,5}$	$r_{1,5}=40q_{1,5}$	$s_{1,5}=r_{1,5}$	0–0.75
0–0.75	1,000/10,000	$p_{1,6}$					
0.75–1.5		$p_{1,7}$	$n_{1,7}=p_{1,7}-p_{1,6}$	$q_{1,7}=n_{1,7}$	$r_{1,7}=200q_{1,7}$	$s_{2,1}=s_{1,5}+r_{1,7}$	0–1.5
0–1.5		$p_{2,1}$					
1.5–3.0		$p_{2,2}$	$n_{2,2}=p_{2,2}-p_{2,1}$	$q_{2,2}=n_{2,2}$	$r_{2,2}=100q_{2,2}$	$s_{2,2}=s_{2,1}+r_{2,2}$	0–3.0
3.0–4.5		$p_{2,3}$	$n_{2,3}=p_{2,3}-p_{2,1}$	$q_{2,3}=q_{2,2}+n_{2,3}$	$r_{2,3}=67q_{2,3}$	$s_{2,3}=s_{2,1}+r_{2,3}$	0–4.5
4.5–6.0		$p_{2,4}$	$n_{2,4}=p_{2,4}-p_{2,1}$	$q_{2,4}=q_{2,3}+n_{2,4}$	$r_{2,4}=50q_{2,4}$	$s_{2,4}=s_{2,1}+r_{2,4}$	0–6.0
6.0–7.5		$p_{2,5}$	$n_{2,5}=p_{2,5}-p_{2,1}$	$q_{2,5}=q_{2,4}+n_{2,5}$	$r_{2,5}=40q_{2,5}$	$s_{2,5}=s_{2,1}+r_{2,5}$	0–7.5
0–7.5	1,000/1,000	$p_{2,6}$					
7.5–15		$p_{2,7}$	$n_{2,7}=p_{2,7}-p_{2,6}$	$q_{2,7}=n_{2,7}$	$r_{2,7}=200q_{2,7}$	$s_{3,1}=s_{2,5}+r_{2,7}$	0–15
0–15		$p_{3,1}$					
15–30		$p_{3,2}$	$n_{3,2}=p_{3,2}-p_{3,1}$	$q_{3,2}=n_{3,2}$	$r_{3,2}=100q_{3,2}$	$s_{3,2}=s_{3,1}+r_{3,2}$	0–30
30–45		$p_{3,3}$	$n_{3,3}=p_{3,3}-p_{3,1}$	$q_{3,3}=q_{3,2}+n_{3,3}$	$r_{3,3}=67q_{3,3}$	$s_{3,3}=s_{3,1}+r_{3,3}$	0–45
45–60		$p_{3,4}$	$n_{3,4}=p_{3,4}-p_{3,1}$	$q_{3,4}=q_{3,3}+n_{3,4}$	$r_{3,4}=50q_{3,4}$	$s_{3,4}=s_{3,1}+r_{3,4}$	0–60
60–75		$p_{3,5}$	$n_{3,5}=p_{3,5}-p_{3,1}$	$q_{3,5}=q_{3,4}+n_{3,5}$	$r_{3,5}=40q_{3,5}$	$s_{3,5}=s_{3,1}+r_{3,5}$	0–75
0–75	10,000/1,000	$p_{3,6}$					
75–150		$p_{3,7}$	$n_{3,7}=p_{3,7}-p_{3,6}$	$q_{3,7}=n_{3,7}$	$r_{3,7}=200q_{3,7}$	$s_{4,1}=s_{3,5}+r_{3,7}$	0–150
0–150		$p_{4,1}$					
150–300		$p_{4,2}$	$n_{4,2}=p_{4,2}-p_{4,1}$	$q_{4,2}=n_{4,2}$	$r_{4,2}=100q_{4,2}$	$s_{4,2}=s_{4,1}+r_{4,2}$	0–300
300–450		$p_{4,3}$	$n_{4,3}=p_{4,3}-p_{4,1}$	$q_{4,3}=q_{4,2}+n_{4,3}$	$r_{4,3}=67q_{4,3}$	$s_{4,3}=s_{4,1}+r_{4,3}$	0–450
450–600		$p_{4,4}$	$n_{4,4}=p_{4,4}-p_{4,1}$	$q_{4,4}=q_{4,3}+n_{4,4}$	$r_{4,4}=50q_{4,4}$	$s_{4,4}=s_{4,1}+r_{4,4}$	0–600
600–750		$p_{4,5}$	$n_{4,5}=p_{4,5}-p_{4,1}$	$q_{4,5}=q_{4,4}+n_{4,5}$	$r_{4,5}=40q_{4,5}$	$s_{4,5}=s_{4,1}+r_{4,5}$	0–750

* In figure 4 (A and B) the bridge ratio is B/A.

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HEATS OF ISOMERIZATION OF THE FIVE HEXANES*

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ABSTRACT

A procedure is outlined and utilized for determining with high precision the ratios of the heats of combustion, and hence the heats of isomerization, of the five hexanes. In principle, the ratio of the heats of combustion of any two isomers was determined as the inverse ratio of the masses of carbon dioxide whose formation in the combustion of the respective hexanes produced identical increases of temperature in the calorimeter system, measured as an increase in the resistance of the platinum resistance thermometer.

The following values were obtained for the liquid state at 25° C, and calculated to the gaseous state at 25° C and 0° K:

Isomer	Heat of isomerization, ΔH For n-C_6H_{14}=i-C_6H_{14}		
	Liquid	Gas	
	25° C	25° C	0° K
	kcal/mole	*kcal/mole*	*kcal/mole*
n-Hexane	0	0	0
2-Methylpentane	−1. 30 ±0. 21	−1. 68 ±0. 23	−1. 04 ±0. 25
3-Methylpentane	−0. 76 ±0. 19	−1. 09 ±0. 21	−0. 42 ±0. 23
2, 3-Dimethylbutane	−1. 96 ±0. 20	−2. 58 ±0. 22	−1. 89 ±0. 24
2, 2-Dimethylbutane	−3. 49 ±0. 18	−4. 44 ±0. 21	−3. 60 ±0. 23

Values for the heats of isomerization for the gaseous state at 600° and 1,000° K were also calculated, utilizing values of $H^\circ - H_0^\circ$ calculated by Pitzer for each of the isomers at these temperatures.

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I. INTRODUCTION

In continuation of the program of determining the heats of formation and of isomerization of the paraffin hydrocarbons [1, 2, 3],[1] calorimetric measurements have been made which yield values for the differences in the heats of combustion of the five hexanes in the liquid state of 25° C. These values, which are also the heats of isomerization in the liquid state at 25° C, have been combined with calculated values for the differences in the heats of vaporization to give values for the heats of isomerization in the gaseous state at 25° C. Combination of these with values for the heat content of the various isomers in the gaseous state as a function of the temperature gives values for the heats of isomerization in the gaseous state at several temperatures from 0° to 1,000° K.

II. UNIT OF ENERGY, MOLECULAR WEIGHTS, ETC.

The unit of energy upon which the values reported in this paper are based is the international joule. For conversion to the conventional artificial, or defined, calorie, the following relation is used [4]:

$$4.1833 \text{ international joules} = 1 \text{ calorie.} \quad (1)$$

The molecular weight of carbon dioxide, the mass of which was used to determine the amount of reaction, was taken as 44.010, from the 1941 table of atomic weights [5].

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [6]. In other cases, reasonable estimates of the uncertainty were made.

III. METHOD AND APPARATUS

1. METHOD

The aim of the experimental part of this investigation was to determine as precisely as possible the values of the ratio of the heat of combustion of each isomer of hexane to that of normal hexane. The difference between unity and the value of this ratio, multiplied by an accepted value for the heat of combustion of normal hexane, gives the

[1] Figures in brackets indicate the literature references at the end of this paper.

difference between the heat of combustion of normal hexane and the given isomer. In principle, the ratio of the heats of combustion of any two isomers was determined as the inverse ratio of the masses of carbon dioxide whose formation in the combustion of the respective hexanes produced identical increases of temperature in the calorimeter system, measured as an increase in the resistance of the platinum resistance thermometer. With this procedure, the energy equivalent of the calorimeter system need be known only approximately, and, in the limiting case where the calorimetric conditions are the same in all experiments for all of the isomers, the energy equivalent need not be known at all.

The method of reducing the experimental observations was as follows: Let

ΔR_c = the corrected increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer at a mean temperature of 26.50° C, as measured with the given resistance bridge;

E_s = the energy equivalent, over a "standard" interval of temperature, of the "standard" calorimeter system, obtained as the ratio of a given quantity of electric energy to the value of ΔR_c produced by it and expressed as international joules per ohm;

E = the energy equivalent of the actual calorimeter system;

Δr_i = the increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the platinum thermometer, produced by the ignition process of heating and burning the iron wire;

Δr_n = the increase in temperature of the calorimeter system, expressed as the increase in resistance in ohms of the platinum thermometer, produced by the formation of the small amount of nitric acid in the combustion;

C = the heat capacity of the amount of hydrocarbon placed in the bomb, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer;

q = the heat evolved, in international joules per gram of carbon dioxide, in the combustion of the hydrocarbon in the bomb process, with the pressure of oxygen, the mass of hydrocarbon, and the mass of water placed in the bomb being substantially the same in all experiments;

m_{CO_2} = the mass of carbon dioxide formed in the combustion of the hydrocarbon; and

δ = a very small correction term, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer, to take account of (a) variations in the mass of the glass ampoule from the "standard" value of 0.20 g, and (b) variations in the mean temperature of an experiment from the "standard" value of 26.50° C.

The following relations hold:

$$E = E_s + C + \delta \tag{2}$$

$$q m_{CO_2} = (\Delta R_c - \Delta r_i - \Delta r_n) E. \tag{3}$$

Eliminating E and solving for q/E_s, which will be called B, there is obtained

$$B=\frac{q}{E_s}=\frac{\Delta R_c}{m_{CO_2}}\left(1+\frac{C+\delta}{E_s}\right)\left(1-\frac{\Delta r_i+\Delta r_n}{\Delta R_c}\right). \quad (4)$$

The terms $(C+\delta)/E_s$ and $(\Delta r_i+\Delta r_n)/\Delta R_c$, which are each small in comparison with unity and have values near 0.00013 and 0.0014, respectively, in all the combustion experiments for all the isomers, substantially cancel in obtaining the ratio of the value of B for one isomer to that for another.

For any two isomers, the ratio of the heats evolved per gram of carbon dioxide is equal to the ratio of their heats of combustion per mole. If the subscripts n and i refer to the normal paraffin and the branched-chain isomer, respectively, and $-\Delta U_B$ is the heat evolved per mole of hydrocarbon on combustion in the bomb process, then

$$(q/E_s)_i/(q/E_s)_n=B_i/B_n=(-\Delta U_B)_i/(-\Delta U_B)_n \quad (5)$$

and

$$(-\Delta U_B)_n-(-\Delta U_B)_i=(-\Delta U_B)_n(1-B_i/B_n). \quad (6)$$

For the reaction

$$n\text{-}C_6H_{14}(\text{liq})=i-C_6H_{14}(\text{liq}), \quad (7)$$

the energy of isomerization at the pressure in the bomb, 30 atm, is

$$\begin{aligned}(U_i-U_n)\ (\text{liq, 30 atm})&=-[(-\Delta U_B)_n-(-\Delta U_B)_i]\\&=-(-\Delta U_B)_n(1-B_i/B_n).\end{aligned} \quad (8)$$

That is, the energy of isomerization of the normal paraffin into the given isomer, for the liquid state at the pressure in the bomb, is equal to a constant, $(\Delta U_B)_n$, multiplied by the difference between unity and the experimentally determined value of the ratio B_i/B_n. Since the energy of isomerization lies in the range from 1 to 5 kcal/mole, while the heat of combustion, $-\Delta U_B$, is near 1,000 kcal/mole, the important advantage of this method of handling the experimental observations is that it retains all the possible precision in getting the energies of isomerization as differences in the heats of combustion, and, further, the absolute value of the heat of combustion of any one isomer need not be known at all accurately. For example, an uncertainty of ½ percent in the value of $(-\Delta U_B)_n$ does not significantly affect the value calculated for a given energy of isomerization. Since in the foregoing equations B is essentially $\Delta R_c/m_{CO_2}$, the important quantity to determine for each isomer is the quotient of the increase in resistance of the given platinum resistance thermometer divided by the corresponding mass of carbon dioxide formed.

2. APPARATUS

(a) CALORIMETER ASSEMBLY

With some changes, the calorimeter assembly was that used in the determination of the heat of formation of sulfur dioxide [7] and a number of subsequent investigations. The detailed description of the characteristics of this type of calorimeter is given by Dickinson

[8]. The jacket, containing approximately 11 liters of water, was maintained near 28° C at a constant temperature within several thousandths of a degree by means of the automatic regulator previously described [9]. For operation when the temperature of the room was above about 26.5° C, ice water was made to siphon at a controlled rate through a coil of copper tubing immersed in the water in the jacket, to provide a slight excess of refrigeration, which was then balanced automatically by the heating device.

The calorimeter can, supported on three pointed ivory pegs, contained 2873.26 g of water, the stirrer, platinum resistance thermometer, heater, and the bomb, which contained the hydrocarbon in a sealed glass ampoule, 1 ml of water, and oxygen to a pressure of 30 atm (calculated to 25° C). With the exception of minor variations in the mass of hydrocarbon and of the glass ampoule, the calorimeter system was the same in all the experiments. The stirrer was operated at a substantially constant rate near 285 rpm with a belt drive from a synchronous motor.

The calorimeter heater was made of a cylinder of thin copper, 7.8 cm in diameter and 7.5 cm in height, coated on the outside with Pizein [9], over which was wound noninductively about 145 ohms of enameled manganin wire, No. 30 AWG. To the ends of the manganin wire were soldered enameled copper wires, No. 24 AWG, serving as current leads. A second layer of Pizein was then applied. Potential leads, of No. 28 AWG enameled copper wire, were soldered to the current leads midway in the air gap between the calorimeter can and the jacket. These four leads, together with the two firing leads from the bomb, were imbedded in a layer of Pizein placed between two plates of mica, the whole being fastened tightly to the metal jacket by means of a metal plate and fastening screw. The cylindrical heater fitted snugly around the body of the bomb.

(b) THERMOMETRIC SYSTEM

A new platinum resistance thermometer of the regular flat calorimetric type [2] was used in conjunction with the new type Mueller resistance bridge,[3] the installation of which was reported previously [10, 11]. The constants of the thermometer (Serial No. 285,380) were determined by the Thermometry Section of this Bureau in terms of NBS international ohms. Using the factor 1.00046 for conversion to absolute ohms,[4] and expressing the resistance, R, as a function of the temperature, t, in degrees centigrade, there is obtained for this thermometer, for the range 0° to 100° C, the relation

$$R=25.5057+0.101420t-0.00001420t^2 \text{ absolute ohms} \qquad (9)$$

and

$$dR/dt=0.101420-0.00002840t. \qquad (10)$$

It should be emphasized that knowledge of the actual relation between resistance and temperature for the given thermometer is not needed for the calorimetric experiments proper, when these are performed over substantially the same interval of resistance at the same mean temperature. Equation 9 is used here only to determine to

[2] Catalog No. 8160, Leeds and Northrup Co., Philadelphia, Pa.
[3] Serial No. 404, Eppley Manufacturing Co., Newport, R. I.
[4] The factor 1.00046 was used in place of the present "best" value of 1.00048 [12, 13] because the values of the resistance coils of the bridge had in manufacture been labeled in absolute ohms derived from the NBS international ohm with the factor 1.00046 [14].

0.01°C the temperature to which the observed thermodynamic quantity is to be assigned. Equation 10 indicates that the value of dR/dt changes by only 0.003 percent for a change of 1°C in the mean temperature. Actually, substantially all of the experiments of the present investigation had mean temperatures within 0.10°C of the selected standard mean temperature, so that this correction would be negligible.

(c) COMBUSTION BOMB

The assembled bomb, shown in figure 1, differs somewhat from those previously described [8, 15, 16, 17, 26, 27]. The body,[5] *A*, is made of

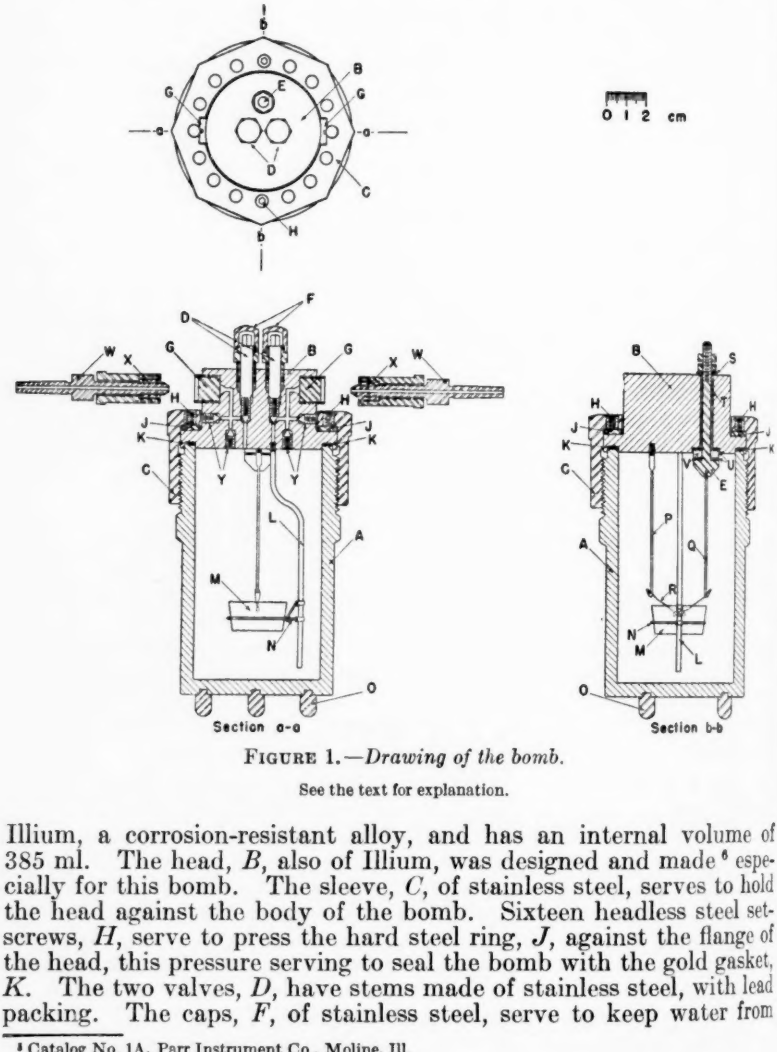

FIGURE 1.—*Drawing of the bomb.*

See the text for explanation.

Illium, a corrosion-resistant alloy, and has an internal volume of 385 ml. The head, *B*, also of Illium, was designed and made[6] especially for this bomb. The sleeve, *C*, of stainless steel, serves to hold the head against the body of the bomb. Sixteen headless steel setscrews, *H*, serve to press the hard steel ring, *J*, against the flange of the head, this pressure serving to seal the bomb with the gold gasket, *K*. The two valves, *D*, have stems made of stainless steel, with lead packing. The caps, *F*, of stainless steel, serve to keep water from

[5] Catalog No. 1A, Parr Instrument Co., Moline, Ill.
[6] American Instrument Co., Silver Spring, Md.

the valves when the bomb is under water. The plugs, *G*, of stainless steel, serve to close the openings to the valves after the bomb is filled with oxygen. The inlet tube, *L*, of platinum, has its end below the platinum cup, *M*, in which is placed the sample to be burned. The cup, *M*, is supported at three points on the ring, *N*, which is made of platinum wire, No. 18 AWG. The electric terminal for ignition, *E*, is made of stainless steel and is insulated from the remainder of the head by means of a Bakelite washer, *S*, a Bakelite sleeve, *T*, and a quartz washer, *V*. The quartz washer, *V*, is bounded by two gold washers, *U*, the upper one being not in direct contact with the insulated terminal. The other electric terminal for ignition is the bomb itself, and the ignition circuit is completed through the platinum wires, *P* and *Q* (No. 18 AWG), and the iron fuse wire, *R* (No. 36 AWG), which latter is held in place by squeezing on it the turned-back ends of the wires *P* and *Q*. The iron fuse wire *R* was made with a central coil and straight ends, as shown in the figure. Permanent plugs, *Y*, close the unneeded openings that were made in producing the inlet and outlet passageways. At the times of emptying the bomb, the connections, *X*, are put in place of the plugs, *G*. The ends, *W*, have a standard, 1 in 10, taper. The bomb is supported by the three stainless steel pegs, *O*, which are 11 mm in height and provide a reasonable clearance underneath the body of the bomb for circulation of the water.

IV. CHEMICAL PROCEDURE

1. PREPARATION OF THE HEXANES

For each of the five isomeric hexanes, small lots of material were obtained from two independent sources.

The first lots each of *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane (hereafter labeled "A" in this paper) were obtained from the Research Laboratories of the General Motors Corporation, through the courtesy of Thomas A. Boyd. The synthesis and purification of these five hexanes have been described by Cramer and Mulligan [18], who reported values for the boiling point, density, and refractive index. Following this, the materials were redistilled from sodium in a small rectifying column by P. L. Cramer, of the General Motors Research Laboratories, and sent to the National Bureau of Standards for this investigation. Before the determination of the heats of combustion of these samples, measurements were made on them of the boiling point, the difference between the temperatures of boiling and condensation, and, for 2-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane, the freezing point, by Wojciechowski, who has reported in detail on these properties [19]. On a small part of each of these samples, measurements were also made of the heat capacity in the range from −185° to 50° C by Stull, who has reported in detail concerning the heat capacities of the solid and liquid states, the heats of fusion for *n*-hexane, 2-methylpentane, and 2,2-dimethylbutane, and the heat of transition for the latter [20].

The second lot of *n*-hexane (labeled "B" in this paper) was obtained from B. J. Mair, of this Bureau, who has described its synthesis, purification, and properties [21].

The second lots each of 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane (labeled "B" in this paper) were obtained from the Experimental Division of the Sun Oil Co., through the courtesy of Johannes H. Bruun. These three hexanes were separated by distillation from a West Virginia natural gasoline by Bruun, Hicks-Bruun, and Faulconer [22], who have described the purification and determined the boiling point, freezing point (for 2–methylpentane and 2,3-dimethylbutane), density, and refractive index.

The second lot of 2,2-dimethylbutane (labeled "B" in this paper) was obtained from the Research Laboratory of the Universal Oil Products Co., through the courtesy of Gustav Egloff and A. V. Grosse. The synthesis and purification of this material have been described by Schmerling, Friedman, and Ipatieff [23] Precise measurements of the refractive index of this material have been obtained by Grosse [24].

In addition to the purification described in the foregoing papers, each of these lots of isomeric hexanes was, before use in the present investigation, filtered through a column of silica gel to remove any possible traces of aromatic hydrocarbons, olefin hydrocarbons, and nonhydrocarbon impurities [25].

No explicit quantitative estimate has been made of the amount of impurity in any of the 10 lots of material measured, except in the case of 2-methylpentane, which was reported by Bruun, Hicks-Bruun, and Faulconer to have a purity greater than 99.99 mole percent [22].

In view of (a) the manner of preparation and purification, (b) the accord of the physical properties of refractive index, density, boiling point, and, where available, the freezing point, with the "best" values recorded in the literature [18, 19, 20, 21, 22, 23, 28], (c) the fact that no significant difference in heat of combustion was observed for the two lots of each of the isomers from independent sources, and (d) the fact that the impurities would be expected to be isomeric hexanes to the presence of which the measurements are not overly sensitive (see following), it may be concluded that the amount of combustible impurity in any of the 10 lots of material was such as to alter the heat of combustion by not more than 5 parts in 100,000. It would be expected from the manner of preparation and purification that the impurities are isomeric hexanes. On this basis, it may be calculated that the amount of one isomer required to be present as impurity in another isomer in order to alter the heat of combustion of the latter by 5 parts in 100,000 (or 0.05 kcal/mole) ranges from a minimum of 1.5 mole percent for the pair, *n*-hexane and 2,2-dimethylbutane (which normally boil 19° C apart), to a maximum of 8 mole percent for the pair, 2-methylpentane and 3-methylpentane (which normally boil 3° C apart).

2. SEALING OF THE HYDROCARBONS IN GLASS AMPOULES

For combustion in the liquid state in the bomb, the hydrocarbons were sealed in thin-walled soft-glass ampoules, which are shown in figure 2 in various stages of preparation. These ampoules differ from those described by Richards and Barry [29], and later by Jessup [30],

in that they are made with two openings, instead of one, in order to facilitate filling. The procedure of making these bulbs is briefly as follows: A round bulb was blown at the end of a tube which had been previously drawn to a thin-walled capillary, as in part 1 of figure 2. The sides of the bulb were then flattened, as in part 2 of figure 2. A second and smaller opening was then made on the bulb by heating a small area and pulling away the glass, producing the form shown in part 3 of figure 2. The capillary tubes were then cut off to the desired lengths and the tube, *A*, was bent, to form the completed bulb as shown in part 4 of figure 2.

After drying in an air oven and blowing out with dry air, the empty bulbs were cooled in a desiccator and afterwards weighed—the average weight of one bulb being about 0.2 g. In filling a bulb with the liquid to be burned, the tip *A* (part 4 of fig. 2) was immersed in the given

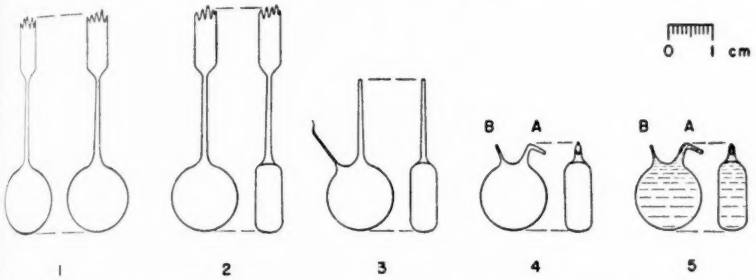

FIGURE 2.—*Drawing illustrating the steps in making and sealing the glass ampoules.*

See the text for explanation.

liquid and a slight suction from a vacuum line was applied at the opening *B* to draw the liquid into the bulb. After filling, the level of the liquid at *A* was drawn inward to a distance of about 4 mm from the tip, by touching a piece of filter paper at the tip *B*. A hot pointed flame was then quickly applied to *A* and the tip sealed, as shown in part 5 of figure 2. As the tip *A* cooled, the level of the liquid at *B* drew away from the tip, usually to a distance of about 3 mm. If the contraction was less than this amount, a piece of ice applied momentarily at the bottom of the bulb served to produce the desired amount of contraction, and the opening at *B* was then sealed, as shown in part 5 of figure 2. The entire process of filling and sealing one bulb may be easily completed in less than one minute. For the hexanes, the mass of hydrocarbon contained in a bulb was about 0.8 g, or 1.2 ml, on the average.

3. IGNITION OF THE HYDROCARBON

For combustion in the bomb, the filled and sealed glass bulb containing the hydrocarbon was laid on one of its two flat sides in the cup, shown at *M* in figure 1. The iron wire fuse, which in the present experiments consisted of a 5-cm length of No. 36 AWG Parr ignition wire,[7] was placed with its central coil (see fig. 1) separated by a space of about 1 mm from the upper flat side of the bulb. An alternating

[7] Catalog No. 45C10, Parr Instrument Co., Moline, Ill.

current at 24 volts, provided by a small transformer on the 110-volt house line, supplied the energy for ignition. At the end of a combustion, the glass of the bulb was found lying at the bottom of the crucible, *M*, in the form of one or more globules, which were clear in some cases and in others darkened by some material distributed through the glass. Following the argument presented by Jessup [30], it was concluded that the quantity of the material, iron oxide or carbon, that produced such darkening was negligible in amount and that the heat effect associated with it was not at all significant. The evaluation of the energy associated with the process of ignition is discussed in Section V–1.

4. PURIFICATION OF THE OXYGEN USED FOR COMBUSTION

The oxygen used for the combustion of the hydrocarbons was ordinary commercial oxygen, which was freed of combustible impurities, following the findings of Keffler [31, 32] and Jessup and Green [15]. The apparatus used in the present investigation for purifying the oxygen and filling the bomb is shown in the upper part of figure 3. *A* is the cylinder containing the oxygen under pressure; *B* is the valve for reducing the pressure to somewhat above 30 atm and for regulating the rate of flow of the oxygen; *C* is a high-pressure steel tube,[8] which is electrically heated and contains copper oxide kept at about 500° C, to oxidize any combustible impurities in the oxygen; *D* is a coil, which may be immersed in water to cool the oxygen issuing from the oxidizing tube, *C; E* is a high-pressure steel tube,[9] which contains Ascarite (a commercial mixture of sodium hydroxide and asbestos) at room temperature to remove all of the carbon dioxide from the oxygen before it passes into the bomb at *G; F* is a Bourdon-type gage for measuring the pressure of the oxygen when the flow of oxygen is stopped and before the bomb is closed. The connecting fittings are of chrome-vanadium steel and the connecting tubing is of chrome-molybdenum steel.

Before each filling, the bomb was flushed with the purified oxygen for 15 minutes at a rate of flow of 400 ml (at room temperature and 1 atm) per minute. Then the exit valve of the bomb was closed and the bomb filled with the purified oxygen at a rate that required 15 minutes to attain the final pressure of 30 atm (calculated to 25° C).

5. EXAMINATION OF THE PRODUCTS OF COMBUSTION

The products of each combustion were examined to determine the amount of carbon dioxide formed in the main reaction of combustion in the bomb, the amount of nitric acid formed by oxidation of some of the nitrogen in the oxygen used for combustion, and the amount of carbon dioxide formed by subsequent oxidation of any products of incomplete combustion.

The analytical train used for determining the carbon dioxide is shown in the lower part of figure 3. *H* is a cylinder (different from *A*) containing oxygen under pressure; *I* is a valve for reducing the pressure to somewhat above 1 atm and for regulating the flow of oxygen; *J* is an electrically heated furnace which maintains at about

[8] Catalog No. 406–31, American Instrument Co.
[9] Catalog No. 406–32, American Instrument Co.

550° C a glass (Corning 172) tube containing copper oxide, to oxidize any combustible impurities in the oxygen; *K* is a tube containing Ascarite, to remove carbon dioxide; *G* is the combustion bomb; *L* is an absorption tube containing anhydrous magnesium perchlorate, backed with a plug of phosphorus pentoxide, to remove water [1]; *M* is a weighed absorption tube containing Ascarite, backed, in order, with plugs of anhydrous magnesium perchlorate and phosphorus

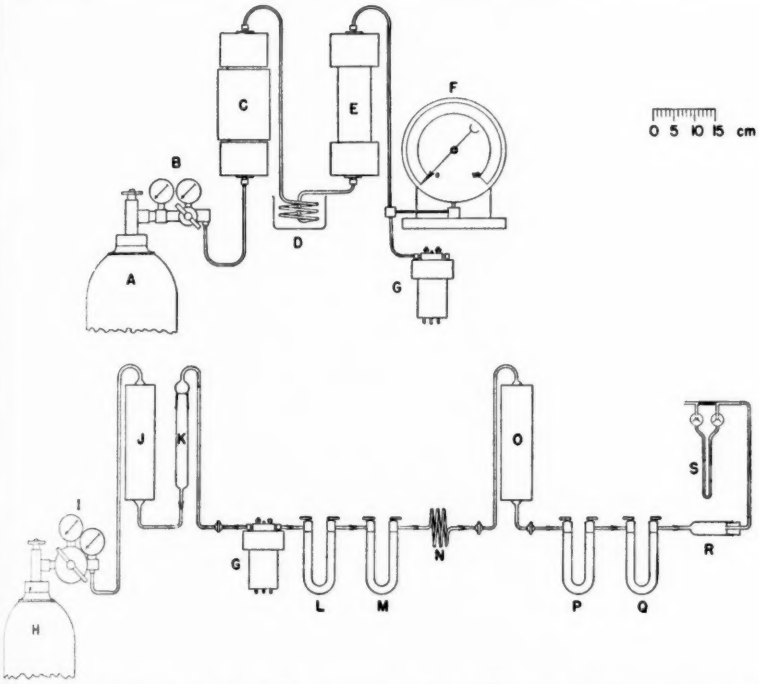

FIGURE 3.—*Diagram showing the apparatus for filling the bomb with purified oxygen and for analyzing the products of combustion.*

See the text for explanation.

pentoxide, to collect the carbon dioxide [1]; *N* is a flexible glass coil to permit coupling of the tube *M* to the fixed tube leading to the electrically heated furnace, *O*, kept at 550° C, which is a duplicate of *J* and serves to oxidize any combustible material remaining in the products of the combustion in the bomb; *P* is an absorption tube similar to *L*; *Q* is a weighed absorption tube similar to *M*; *R* is a guard tube containing, in order, phosphorus pentoxide, magnesium perchlorate, and Ascarite, to prevent back-diffusion of water vapor or carbon dioxide into the tube *Q* from the air; *S* is a calibrated flow meter, discharging to the air of the room, which is used to measure the rate of flow of the oxygen through the system. The analytical train just described is all glass from the valve, *I*, to the guard tube, *R*, with the exception of the metal bomb, *G*, and its metal tapered connections (shown in detail at *W*, *X* in fig. 1).

During the period in which, immediately preceding examination of the products of combustion, the analytical train is being flushed with purified oxygen, a straight open tube with appropriate tapered ends serves as a "stand-in" for the bomb at *G*. The analytical train is first flushed with oxygen with the connection between *N* and *O* open for about 5 minutes, in order to displace into the air of the room, instead of into the hot furnace *O*, the hydrogen with which the tube *M* had been filled for purposes of weighing. After a calorimetric combustion experiment has been completed and the analytical train has been flushed with purified oxygen, the bomb is put in place of the "stand-in" tube in the analytical train, as shown at *G* in the lower part of figure 3. The exit valve of the bomb is then carefully opened, and the gaseous products of combustion are permitted to issue from it at a rate of about 200 ml (measured at 1 atm and room temperature) per minute. After the pressure in the bomb is reduced to 1 atm and the flow of gas has stopped, the inlet valve of the bomb is opened and purified oxygen is passed through the bomb at about the same foregoing rate for about 1 hour. The absorption tubes *M* and *Q* are then appropriately weighed to determine, respectively, the amount of carbon dioxide formed in the main reaction and the amount of carbon dioxide, if any, formed in the subsequent combustion in the tube *O* of any products of incomplete combustion in the bomb. "Blank" determinations of the changes in weight of the absorption tubes *M* and *Q*, made with the same quantity of oxygen passing through the system as in an actual experiment, indicated, within ± 0.00010 g, zero change in the weight of the main tube, *M*, and a change of 0.00010 to 0.00030 g in the weight of the second tube, *Q*. Appropriate corrections for this latter were made to determine the amount of carbon dioxide formed in the subsequent combustion of the products of incomplete combustion, if any. The mass of carbon dioxide collected in the main tube, *M*, was near 2.5 g, on the average. In connection with this method of determining the amount of carbon dioxide formed in the combustion in the bomb, Jessup [30] has shown that no significant amount of nitric acid is removed from solution in the water in the bomb by the indicated quantity of gas issuing from the bomb. This is in accord with calculations made by the authors.

The procedure of handling the absorption tubes *M* and *Q* was that previously described [1, a], with the tubes filled with dry hydrogen at the times of weighing.

The small amount of nitric acid, formed through oxidation of some of the nitrogen in the oxygen used for combustion and its subsequent reaction with an absorption in water, was determined after the removal of the gaseous products of combustion from the bomb by carefully washing the inside of the bomb with water and titrating the aqueous solution with standard 0.1 *N* aqueous sodium hydroxide.

Occasionally, there occurred an abnormal combustion in which there was formed a relatively large amount of products of incomplete combustion, as measured by the amount of carbon dioxide collected in the second weighed absorption tube (*Q* in fig. 3). Such an abnormal experiment was also usually made evident by a higher than normal rate of combustion. It was concluded that in such experiments the glass ampoule containing the hydrocarbon must have been broken prematurely, so that at the time of ignition the bomb was filled with a

combustible mixture in the gas phase, which produced the accelerated combustion. In several other experiments, which otherwise appeared normal, small but significant amounts of unburned carbon, estimated to be from 0.1 to 0.4 percent of the total, were found in the bomb after combustion. All such abnormal experiments were discarded because either or both the nature and the amount of reaction which actually occurred in the bomb could not be specified.

6. DETERMINATION OF THE AMOUNT OF REACTION

For each calorimetric combustion experiment, the amount of reaction was determined from the mass of carbon dioxide formed, taking 1 mole (44.010 g) of carbon dioxide as equivalent to one-sixth mole of hexane. With this procedure, it becomes unnecessary to determine and correct for the amount of air and water that may be dissolved in the hydrocarbons. Unless precautions are taken to exclude them, air and water may each dissolve in typical hydrocarbons to the extent of several parts in 10,000 by weight.[10] In humid weather, it is practically impossible to prepare sealed bulbs containing water-free hydrocarbons.

For those experiments in which the bulbs were filled in dry weather and in which the combustion was normal, the ratio of the mass of hydrocarbon to the mass of carbon dioxide produced had a value equal to that required stoichiometrically, within one or two parts in 10,000, when due allowance was made for air dissolved in the hydrocarbon.

V. CALORIMETRIC PROCEDURE

1. DETERMINATION OF THE IGNITION ENERGY

The energy added to the calorimeter by the melting and burning of the iron fuse wire was determined in a series of blank experiments in which the calorimeter was at a temperature slightly below that of the jacket, and in which the bomb was charged with purified oxygen to a pressure of 30 atm as in a regular combustion experiment. There were determined the corrected increase in resistance of the platinum resistance thermometer produced by the addition of the ignition energy to the standard calorimeter system, and the mass of any iron wire unburned. Correction to a standard amount of iron wire burned was made using the value 6.63 kilojoules/g for the heat of combustion of the iron wire in oxygen in the bomb.

In table 1 are given the results of 10 experiments to determine the increase in temperature of the standard calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer, produced by the standard ignition process. In table 1, the various columns give, respectively, the number of the experiment; the mass of iron wire burned; Δr_t, the corrected increase in temperature of the standard calorimeter system, expressed as the increase in resistance in ohms of the platinum resistance thermometer; the correction to the standard amount of iron wire burned, 0.00760 g; the value of Δr_t for the standard ignition process, in ohms; and the deviation from the mean. The energy of this standard ignition process is about

[10] See, for example, Moore, Renquist, and Parks [33].

1/700th of the heat evolved in a calorimetric combustion experiment. In determining the absolute value of the heat of combustion of a given hydrocarbon, the entire energy of the ignition process is significant; but in determining the ratios of the heats of combustion of various isomers, as in the present investigation, the energy of ignition substantially cancels because it is in all experiments nearly a constant fraction of the total heat evolved.

TABLE 1.—*Results of the experiments to determine the change in temperature of the standard calorimeter system produced by the standard ignition process*

Experiment	Mass of iron wire burned	Δr_i	Correction to 0.00760 g, wire burned	Δr_i for the standard ignition process	Deviation from mean
	g	*Ohm*	*Ohm*	*Ohm*	*Ohm*
1	0.00774	0.000413	−0.000007	0.000406	−0.000005
2	.00763	.000417	−.000001	.000416	.000005
3	.00773	.000408	−.000006	.000402	−.000009
4	.00774	.000422	−.000007	.000415	.000004
5	.00782	.000427	−.000011	.000416	.000005
6	.00771	.000411	−.000005	.000406	−.000005
7	.00774	.000417	−.000007	.000410	−.000001
8	.00779	.000423	−.000009	.000414	.000003
9	.00759	.000407	.000000	.000407	−.000004
10	.00775	.000420	−.000007	.000413	.000002
Mean				0.000411	
Standard deviation of the mean				$\pm 0.000001_6$	

2. COMBUSTION EXPERIMENTS

The following procedure was followed in performing a calorimetric combustion experiment: The two absorption tubes for carbon dioxide (*M* and *Q* in fig. 3) were prepared, flushed with hydrogen, and weighed [1a, 34]. The sealed glass bulb (part 5 in fig. 2) containing the hydrocarbon, and the iron fuse wire, were weighed and then placed in position below the head of the bomb (see fig. 1). One milliliter of water was placed in the bottom of the body of the bomb. The head of the bomb, *B*, carrying the gold gasket, *K*, in its groove, was placed in position on the body. The hard steel ring, *J*, was placed on the head, and the stainless steel collar, *C*, was screwed by hand down on the body over the head. The collar, *C*, was then screwed back an amount equal to about 2 mm on the periphery. The actual sealing of the bomb to pressure was accomplished by screwing down the 16 set screws, *H*, through the collar against the steel ring, *J*. These screws were tightened gradually, by means of a hexagon socket setscrew wrench, in the usual manner of proceeding from a given setscrew to the one most distant from it, then to that one of the remaining setscrews most distant from the preceding one, and so on. The bomb was placed in the position shown at *G* in the upper part of figure 3, purified oxygen was passed through it for 15 minutes, the exit valve was closed, and the bomb was filled, to a pressure of 30-atm at 25° C, in a period of 15 minutes. After equilibrium was established and the pressure in the bomb adjusted to the standard value, the inlet valve of the bomb was closed. The standard mass of water, 2873.26 ±0.02 g, was weighed in the calorimeter can on the pan of a 5-kg balance having a sensitivity

for this load of 0.008 g per scale division. The calorimeter can was placed in the calorimeter and the bomb was lowered into it, with the electric heating coil in position around the body of the bomb, and the calorimeter can was covered.

With the temperature of the jacket of the calorimeter maintained constant at 28.02° C within about ±0.002° C, the combustion experiments were performed with an initial temperature near 25.00° C and a final temperature slightly below the temperature of the jacket. The calorimetric observations were as usual divided into three parts: (a) a "fore" period of 20 minutes, in which observations were made every 2 minutes; (b) a "reaction" period of 16 minutes, in which the combustion occurred, followed by a reestablishment of thermal equilibrium in the calorimeter; and (c) an "after" period of 20 minutes, in which observations were made every 2 minutes. In the first 5 minutes of the "reaction" period, observations were made of the time, to the nearest second, at which the resistance of the thermometer attained certain preselected values. At these given times, marked by audible seconds signals, observations were made of the deflection on the galvanometer scale. In this way, there was easily obtained, during the period when the temperature of the calorimeter was changing at the rapid rate of 0.004 ohm (0.04° C) per second, the resistance on the given audible second without the necessity of watching the galvanometer scale and the clock simultaneously. During this 5-minute interval, observations were made for the following values of resistance, in ohms, on the bridge: 28.04 (on the 20th minute), 28.05, 28.10, 28.15, 28.20, 28.25, 28.28, 28.30, 28.31, 28.32, and 28.32 (on the 25th minute). These intervals in °C are, respectively, 0.1, 0.5, 0.5, 0.5, 0.5, 0.3, 0.2, 0.1, 0.1, and 0.0. During the last 11 minutes of the "reaction" period, when the temperature change was very small, observations were made every minute. At the end of the "after" period, the temperature of the jacket was measured with the calorimeter thermometer. Upon completion of the calorimetric observations, the bomb was placed in the analytical train, as shown at *G* in the lower part of figure 3, and determination was made of the amount of reaction and of the amount of incomplete combustion, if any.

The value of ΔR_c (see section III–1) was determined as described on page 610 of reference [35] and page 17 of reference [34], with the value being retained in ohms at a given mean temperature instead of being converted to degrees. The average temperature, with respect to time, of the calorimeter during the "reaction" period was determined from a time-temperature plot, using 20-second intervals for the first 5 minutes and longer intervals for the remaining time. If the mean of the initial and final temperatures of the experiment differs significantly from the standard mean temperature, the observed value of ΔR_c needs (a) to be increased by 3 parts per million for each 0.1° C (~ 0.01 ohm) positive difference between such mean temperatures, due to the change in the value of dR/dt (see eq 10), and (b) to be increased by 5 parts per million for the same departure from the standard mean temperature due to the change in the energy equivalent of the calorimeter system with temperature.

3. CORRECTION FOR THE FORMATION OF NITRIC ACID

The value of Δr_n (see section III–1), which is the rise in temperature of the calorimeter system produced by the heat evolved in the formation of a small amount of nitric acid, according to the reaction

$$1/2\ N_2\ (g)+1/2\ H_2O(liq)+5/4\ O_2\ (g)=HNO_3(aq), \qquad (11)$$

was calculated from the amount of nitric acid formed, determined as described in section IV–5, using the value 57.8 kj/mole for the heat evolved in the formation of dilute aqueous nitric acid in the bomb process. In determining the absolute value of the heat of combustion of a given hydrocarbon, the entire energy associated with the formation of nitric acid is significant; but in determining the ratios of the heats of combustion of various isomers, the value of Δr_n substantially cancels because it is in all experiments nearly a constant fraction (0.0001) of the value of ΔR_c.

VI. RESULTS OF THE PRESENT INVESTIGATION

The experimental results of the present investigation, giving values of $B=q/E_s$ as defined by eq 4, are presented in tables 2, 3, 4, 5, and 6 for *n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane, respectively. The symbols at the heads of the columns in these tables are defined in section III–1 of this paper, on page 610 of reference [35], or on page 17 of reference [34]. In 6 of the 48 experiments, as indicated in the footnotes marked "b" in tables 3, 4, and 6, a correction (plus) was made to the observed value of ΔR to take account of a small amount of incomplete combustion, determined as described in section IV–5 of this paper. This correction is concerned only with the deficiency in heat energy resulting from the small amount of incomplete combustion, and its value was calculated on the assumption that the product of incomplete combustion was carbon monoxide. If some of the hydrogen in the original hydrocarbon was not completely oxidized to water, the correction as made would be too small. In these six experiments, the number of moles of hydrocarbon participating in the combustion was measured stoichiometrically by adding the small amount of carbon dioxide (collected in tube *Q*, fig. 3) to the principal amount of carbon dioxide (collected in tube *M*, fig. 3).

TABLE 2.—*n-Hexane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B[a]	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
1A	2.26163	0.001927	0.001915	0.000138	0.258934	0.000416	0.000028	0.1143064	−0.0000248
2A	2.23988	.001930	.001974	.000094	.256553	.000398	.000027	.1143604	.0000292
3A	2.33612	.001930	.001639	.000107	.267541	.000428	.000027	.1143420	.0000108
4A	2.61928	.001935	.000785	.000080	.299854	.000413	.000028	.1143292	−.0000020
5B	2.46001	.001929	.001255	.000115	.281662	.000415	.000027	.1143314	.0000002
6B	2.50299	.001940	.001122	.000130	.286537	.000418	.000027	.1143155	−.0000157
7B	2.63480	.001931	.001019	.000098	.301673	.000421	.000027	.1143426	.0000114
8B	2.64505	.001932	.001007	.000152	.302876	.000417	.000028	.1143553	.0000241
9B	2.69685	.001929	.000854	.000131	.308690	.000417	.000028	.1143160	−.0000152
10B	2.72779	.001943	.000741	.000114	.312217	.000416	.000028	.1143136	−.0000176
Mean								0.1143312	
Standard deviation of the mean								±0.0000059	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 3.—*2-Methylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B[a]	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
1A	2.44276	0.001942	0.001334	0.000171	0.279250	0.000419	0.000028	0.1141491	−0.0000325
2A	2.62544	.001943	.001009	.000206	.300232	.000399	.000028	.1142093	.0000277
3A	2.47285	.001948	.001178	.000213	.282802	.000409	.000027	.1142021	.0000205
4A	2.65991	.001940	.000609	.000221	.304179	.000411	.000034	[b].1142134	.0000318
5A	2.38014	.001930	.001642	.000042	.272217	.000414	.000079	.1141763	−.0000053
6B	2.50963	.001931	.001064	.000227	.286905	.000420	.000027	.1141597	−.0000219
7B	2.44313	.001939	.001298	.000242	.279363	.000410	.000026	.1141834	.0000018
8B	2.61464	.001941	.001023	.000242	.298831	.000423	.000030	[b].1141591	−.0000225
Mean								0.1141816	
Standard deviation of the mean								±0.0000087	

[a] Corrected to the standard calorimetric system and to 28.00° C.
[b] Corrected (see text, section VI) for a small amount of incomplete combustion: 0.004 percent in 4A and 0.019 percent in 8B.

TABLE 4.—*3-Methylpentane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_c	Δr_i	Δr_n	B[a]	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm/g* CO_2	*Ohm/g* CO_2
1A	2.65080	0.001936	0.000606	0.000208	0.303251	0.000415	0.000029	0.1142505	0.0000069
2A	2.54536	.001942	.000974	.000166	.291060	.000355	.000032	.1142152	−.0000284
3A	2.40361	.001947	.001357	.000226	.274907	.000390	.000030	.1142121	−.0000315
4A	2.61428	.001678	.000760	.000109	.299238	.000410	.000088	.1142886	.0000450
5B	2.47586	.001944	.001165	.000107	.283166	.000420	.000030	[b].1142120	−.0000316
6B	2.46867	.001946	.001174	.000213	.282435	.000412	.000030	.1142439	.0000003
7B	2.48404	.001952	.001088	.000205	.284210	.000406	.000030	[b].1142632	.0000196
8B	2.65221	.001948	.000569	.000190	.303345	.000332	.000032	.1142562	.0000126
9B	2.29533	.001946	.001455	.000179	.262662	.000419	.000028	.1142527	.0000091
10B	2.71964	.001955	.000676	.000179	.311121	.000409	.000030	.1142558	.0000122
11B	2.48216	.001942	.001232	.000101	.284002	.000418	.000084	.1142297	−.0000139
Mean								0.1142436	
Standard deviation of the mean								±0.0000073	

[a] Corrected to the standard calorimetric system and to 28.00° C.
[b] Corrected (see text, section VI) for a small amount of incomplete combustion: 0.006 percent in 5B and 0.007 percent in 7B.

TABLE 5.—*2,3-Dimethylbutane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_e	Δr_i	Δr_n	B [a]	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*/*g* CO_2	*Ohm*/*g* CO_2
1A	2.38849	0.001937	0.001421	0.000130	0.272939	0.000418	0.000030	0.1141003	−0.0000038
2A	2.70214	.001947	.000689	.000106	.308700	.000414	.000030	.1140979	−.0000062
3A	2.43248	.001939	.001243	.000107	.278041	.000411	.000029	.1141389	.0000348
4A	2.61965	.001939	.000665	.000123	.299279	.000403	.000030	.1140979	−.0000062
5A	2.65276	.001937	.000798	.000024	.303209	.000414	.000089	.1141297	.0000256
6B	2.49910	.001943	.000996	.000104	.285491	.000417	.000029	.1140777	−.0000264
7B	2.42879	.001940	.001241	.000152	.277448	.000402	.000028	.1140717	−.0000324
8B	2.28523	.001939	.001383	.000139	.261198	.000410	.000030	.1141206	.0000165
9B	2.35109	.001930	.001508	.000155	.268781	.000413	.000028	.1141492	.0000451
10B	2.50122	.001940	.001039	.000120	.285752	.000409	.000030	.1140874	−.0000167
11B	2.45434	.001938	.001414	.000083	.280441	.000414	.000085	.1140737	−.0000304
Mean								0.1141041	
Standard deviation of the mean								±0.0000081	

[a] Corrected to the standard calorimetric system and to 28.00° C.

TABLE 6.—*2,2-Dimethylbutane*

Experiment	Mass of carbon dioxide formed	k	K	U	ΔR_e	Δr_i	Δr_n	B [a]	Deviation from mean
	g	*min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*	*Ohm*/*g* CO_2	*Ohm*/*g* CO_2
1A	2.42873	0.001955	0.001282	0.000102	0.277138	0.000413	0.000028	0.1139426	0.0000144
2A	2.35890	.001942	.001184	.000114	.269227	.000410	.000028	.1139627	.0000345
3A	2.34257	.001947	.001273	.000123	.267265	.000421	.000029	[b].1139203	−.0000079
4B	2.51852	.001947	.001008	.000112	.287345	.000412	.000030	.1139345	.0000063
5B	2.50422	.001947	.001023	.000122	.285653	.000412	.000030	[b].1139146	−.0000135
6B	2.55891	.001947	−.000082	.000125	.291843	.000414	.000030	.1138983	−.0000298
7B	2.45337	.001945	.001190	.000120	.279934	.000421	.000028	.1139347	.0000065
8B	2.38917	.001942	.001385	.000114	.272578	.000413	.000032	.1139177	−.0000108
Mean								0.1139282	
Standard deviation of the mean								±0.0000070	

[a] Corrected to the standard calorimetric system and to 28.00° C.
[b] Corrected (see text, section VI) for a small amount of incomplete combustion: 0.0026 percent in 3A and 0.005 percent in 5B.

In table 7 are given for the five isomers of hexane values for the following: the constant B in ohms/g CO_2, as defined by eq 4; the ratio of the heat evolved, per mole of hydrocarbon, in the bomb process at 28° C for each isomer to that for *n*-hexane; the difference, between *n*-hexane and each isomer, in the heat of combustion in the bomb process at 28° C; and the heat of isomerization, for the liquid state at 25° C and 1 atm, of *n*-hexane into each isomer. In obtaining the value of $(-\Delta U_B)_n-(-\Delta U_B)_i$, as given in the fourth column, from the experimentally determined values of B_n/B_i and eq 6, the value of $(-\Delta U_B)_n$ for the bomb process at 28° C was taken as 4,152 kj/mole of *n*-hexane, from the work of Jessup [30]. As previously pointed out, the present method of calculating the results is quite insensitive to an error in the value used for $(-\Delta U_B)_n$. For example, an uncertainty of as much as ½ percent in $(-\Delta U_B)_n$ will produce an uncertainty of only ±17 cal/mole in the largest heat of isomerization (*n*-hexane to

2,2-dimethylbutane), which is to be compared with the assigned uncertainty of about 10 times this amount. The values in column 5 differ from those in column 4 because of the difference in the heat capacities of the several isomeric hexanes in the liquid state over the range 25° to 28° C. While not actually significant here, these differences were made for the sake of completeness. Both the Washburn conversion to zero pressure [43] and the conversion of ΔU to $(\Delta U+PV)=\Delta H$ are the same for the several isomers.

TABLE 7.—*Heats of isomerization of the five hexanes in the liquid state* [a]

Substance	B at 28.00° C	Ratio of the heats of combustion in the bomb process B_i/B_n at 28.00° C	Difference in the heats of combustion in the bomb process [b] $(-\Delta U_B)_n-(-\Delta U_B)_i$ at 28.00° C	Heat of isomerization of the liquid $H_i^\circ(\text{liq})-H_n^\circ(\text{liq})$ at 25.00° C	
	Ohm/g CO_2		*kj/mole*	*kj/mole*	*kcal/mole*
n-Hexane	0.1143312 ±0.0000118	1.000000	0	0	0
2-Methylpentane	.1141816 ±0.0000174	0.998692 ±0.000210	5.43 ±0.87	−5.44 ±0.87	−1.30 ±0.21
3-Methylpentane	.1142436 ±0.0000146	.999234 ±0.000188	3.18 ±0.78	−3.16 ±0.78	−0.76 ±0.19
2,3-Dimethylbutane	.1141041 ±0.0000162	.998014 ±0.000200	8.25 ±0.83	−8.25 ±0.83	−1.96 ±0.20
2,2-Dimethylbutane	.1139282 ±0.0000140	.996475 ±0.000183	14.64 ±0.76	−14.61 ±0.76	−3.49 ±0.18

[a] All the uncertainties given in this table are equal to twice the standard deviation [6]. The uncertainty to be assigned to the value for the heat of isomerization of any one of the isomers into any other one is substantially the same as that for the isomerization of *n*-hexane into any one of the isomers, namely, about ±0.19 kcal/mole for the liquid at 25° C.

[b] Obtained by subtracting the value in column 3 from unity and multiplying with the factor 4152 (see sections III-1 and VI).

In table 8 are given values for the following: the heat of isomerization, for the liquid state at 25° C, of *n*-hexane into each isomer, as given in table 7; the difference, between *n*-hexane and each isomer, in the heat of vaporization at 25° C for the gas in the ideal state; and, finally, the heat of isomerization, for the ideal gaseous state at 25° C, of *n*-hexane into each isomer. The values given in table 8 for the difference in the heats of vaporization are taken from a study and correlation that are being made [42] of all the available data for all of the paraffin hydrocarbons.

TABLE 8.—*Heats of isomerization of the five hexanes in the gaseous state* [a]

Substance	Heat of isomerization of the liquid $H_i^\circ(\text{liq})-H_n^\circ(\text{liq})$ at 25° C		Difference in the heats of vaporization $(\Delta H^\circ\ \text{vap})_n-(\Delta H^\circ\ \text{vap})_i$ at 25° C	Heat of isomerization of the gas $H_i^\circ(\text{g})-H_n^\circ(\text{g})$ at 25° C
	kj/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
n-Hexane	0	0	0	0
2-Methylpentane	−5.44 ±0.87	−1.30 ±0.21	0.38 ±0.10	−1.68 ±.023
3-Methylpentane	−3.16 ±0.78	−0.76 ±0.19	.33 ±0.10	−1.09 ±0.21
2,3-Dimethylbutane	−8.25 ±0.83	−1.96 ±0.20	.62 ±0.10	−2.58 ±0.22
2,2-Dimethylbutane	−14.61 ±0.76	−3.49 ±0.18	.95 ±0.10	−4.44 ±0.21

[a] The uncertainty to be assigned to the value for the heat of isomerization of any one of the isomers into any other one is substantially the same as that for the isomerization of *n*-hexane into any one of the other isomers, namely, about ±0.22 kcal/mole for the gas at 25° C.

VII. DATA OF PREVIOUS INVESTIGATIONS

The heats of combustion of only two of the five isomers of hexane have ever before been measured. Data on *n*-hexane were reported by Stohmann, Kleber, and Langbein [36] in 1891, by Zubow [37] in 1898, and by Jessup [30] in 1937, and on 2,3-dimethylbutane by Thomsen [38] in 1886. Since no one investigator measured both isomers, and since the older work of Stohmann et al., Zubow, and Thomsen carries uncertainties as large as several kilocalories per mole, any values deduced from these data for the heat of isomerization of *n*-hexane into 2,3-dimethylbutane would have uncertainties as large as, or larger than, the heat of isomerization itself. For example, the data of Thomsen's seven experiments on 2,3-dimethylbutane yield a value for its heat of combustion having an uncertainty [6] of about 2.5 kcal/mole, whereas the entire value of the heat of isomerization itself as determined in the present investigation is 2.58 ± 0.22 kcal/mole for the gaseous state.

VIII. HEATS OF ISOMERIZATION AS A FUNCTION OF THE TEMPERATURE

Pitzer [39] has calculated, for each of the five hexanes in the ideal gaseous state at 298.16°, 600°, and 1,000° K, values of $H°-H°_0$, the heat content at the given temperature less the heat content at 0° K.

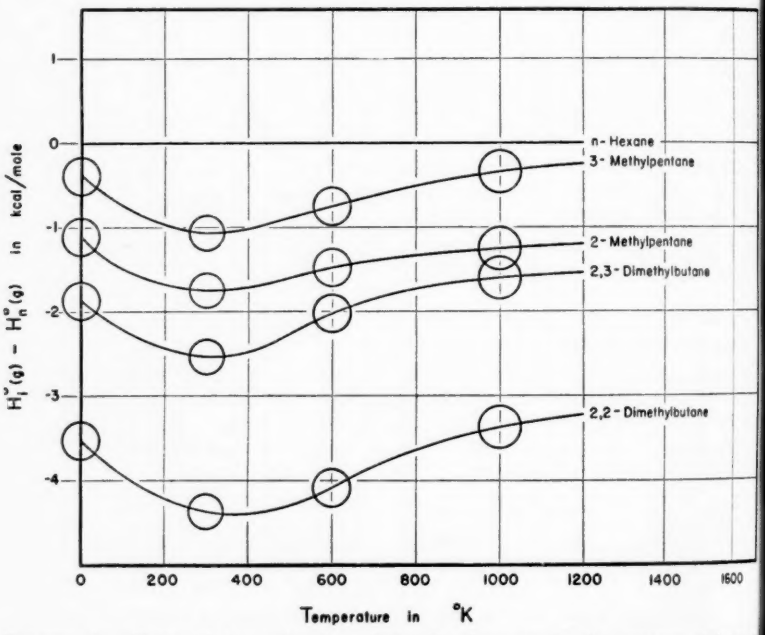

FIGURE 4.—*Heats of isomerization of the five hexanes in the gaseous state as a function of the temperature.*

The scale of ordinates gives, in kcal/mole, the value of ΔH for the isomerization in the gaseous state of *n*-hexane into each of its isomers. The scale of abscissae gives the temperature in ° K.

With these values, the heats of isomerization in the gaseous state may be calculated for these temperatures and 0° K from the values given for 25° C in table 8. The heats of isomerization so calculated are given in table 9 for 0°, 298°, 600°, and 1,000° K, and are presented graphically in figure 4.

TABLE 9.—*Heats of isomerization of the five hexanes in the gaseous state at a number of temperatures from 0° to 1,000° K*

[n-$C_6H_{14}(g) = i$-$C_6H_{14}(g)$; $\Delta H = H^\circ_i(g) - H^\circ_n(g)$]

Substance	Temperature in °K			
	0°	298°	600°	1,000°
	$H^\circ_i(g) - H^\circ_n(g)$			
	kcal/mole	*kcal/mole*	*kcal/mole*	*kcal/mole*
n-Hexane	0	0	0	0
2-Methylpentane	−1.04±0.25	−1.68±0.23	−1.40±0.25	−1.18±0.28
3-Methylpentane	−0.42±0.23	−1.09±0.21	−0.78±0.23	−0.36±0.26
2,3-Dimethylbutane	−1.89±0.24	−2.58±0.22	−2.05±0.24	−1.63±0.27
2,2-Dimethylbutane	−3.60±0.23	−4.44±0.21	−4.16±0.23	−3.44±0.26

IX. DISCUSSION

Values for the heats of formation of the paraffin hydrocarbons are important for two reasons: (1) they may be combined with values of the free energy function, $(F^\circ - H^\circ_0)/T$, calculated statistically, to obtain values for the free energies of formation; (2) they may be studied theoretically from the standpoint of the influence of various substituent alkyl groups on the magnitude of the total energy of the molecule and of the energies of the carbon-hydrogen and carbon-carbon bonds in these molecules.

Considering the present data on the hexanes in relation to the previously reported data on the butanes and pentanes [4], it appears that values for the heptanes and octanes will be required before a complete analysis can be made of the energies of isomerization of all the paraffin hydrocarbons within the limits of uncertainty of present-day measurements. Such determinations on the heptanes [40, 41] and the octanes [40] are now being made.

From the values presented in table 9, it may be seen that with regard to the energy content at 0° K, for the gas having no translational, no rotational, and only the zero-point vibrational energy, the isomers arrange themselves in order of increasing stability, as follows: n-hexane, 3-methylpentane, 2-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

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THE SYSTEM $2CaO.SiO_2$-$K_2O.CaO.SiO_2$, AND OTHER PHASE-EQUILIBRIUM STUDIES INVOLVING POTASH

By William C. Taylor

ABSTRACT

This investigation is one of a series of studies undertaken for the purpose of determining the manner in which K_2O is combined in portland cement clinker. The present research on the phase-equilibrium relations of $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ was made after preliminary examinations had shown that the compound $K_2O.Al_2O_3$ was unstable in the presence of $3CaO.SiO_2$ and $2CaO.SiO_2$. The compounds $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ were found to form a binary system containing one additional compound having a probable composition of $K_2O.23CaO.12SiO_2$. Thermal, optical, and X-ray diffraction data are presented and a temperature concentration diagram has been constructed. The stability of the compound $K_2O.23CaO.12SiO_2$ in portland cement clinker prepared only from K_2O, CaO, Al_2O_3, SiO_2, and Fe_2O_3 has been indicated. While no evidence of any other compound of potash in such preparations, heated and cooled under equilibrium conditions, has been obtained, it has been indicated, in the continuation of this series of investigations, that SO_3 present in a mixture combines with K_2O to form K_2SO_4. This compound has since been observed in many commercial clinkers.

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I. INTRODUCTION

A prominent part of the program of the Portland Cement Association Fellowship at the National Bureau of Standards has, for several years, been devoted to the purpose of establishing the constitution of portland cement clinker. Numerous other workers also have contributed largely to the present general conception of the constitution, which is fairly definite with reference to the principal oxides, namely,

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CaO, MgO, SiO_2, Al_2O_3, and Fe_2O_3. In order to make this concept more definite, it is necessary to have knowledge not only of the phase equilibrium relations among the principal oxides but also those of K_2O, Na_2O, SO_3, and other minor oxides.

The complications usually attending the study of multiple-component systems may be reduced in investigations of the effects of the minor oxides on clinker constitution as follows: First, by conducting a series of investigations on binary and ternary systems in which one of the minor oxides and one or more of the major oxides appear; second, by examining the products of reactions involving one of the minor oxides and one or more of the established clinker compounds. Potash was the minor oxide used in the series of studies reported in the present paper.

Brownmiller [1][1] found that $K_2O.Al_2O_3$ is the only compound of potash which is stable at the liquidus, in the portion of the K_2O-CaO-Al_2O_3 system which he studied. The present author [2] showed that the compound $K_2O.Al_2O_3$ is stable in the presence of $4CaO.Al_2O_3.Fe_2O_3$ and, furthermore, that $K_2O.Al_2O_3$ can exist in the presence of $2CaO.Fe_2O_3$, which may be present in clinkers having an Al_2O_3:Fe_2O_3 ratio less than 0.64. Obviously the stability or instability of $K_2O.Al_2O_3$ in the presence of other cement compounds, such as $2CaO.SiO_2$ and $3CaO.SiO_2$, must be determined; and if new potash compounds should be formed, their phase-equilibrium relations to the various clinker constituents must also be investigated.

The choice of the system $2CaO.SiO_2$-$K_2O.CaO.SiO_2$ for investigation was made after preliminary work indicated that $K_2O.Al_2O_3$ reacts with $2CaO.SiO_2$ and $3CaO.SiO_2$ to form an unidentified potash-lime-silica compound and that $K_2O.Al_2O_3$ and $2CaO.SiO_2$ do not form a binary system. Mixtures along the join $2CaO.SiO_2$-$K_2O.CaO.SiO_2$ in the system K_2O-CaO-SiO_2 are just beyond that portion of the system investigated by Morey, Kracek, and Bowen [3]. These investigators report that the primary phase $2CaO.SiO_2$ appears in the field adjacent to that of $K_2O.CaO.SiO_2$ and that "there is some indication that the index of $2CaO.SiO_2$ in this region is lowered slightly by solid solution, but this is not certain." Thus the possibility remains that some compound exists which is similar to $2CaO.SiO_2$ in appearance but between $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ in composition. In preliminary experiments by the author, free CaO was always found by microscopical examination in heated charges when mixtures of CaO and SiO_2 in molar ratios greater than 2:1, respectively, had been added to $K_2O.CaO.SiO_2$.

II. EXPERIMENTAL METHOD

For the study of the system $2CaO.SiO_2$-$K_2O.CaO.SiO_2$, and for the preliminary experiments reported in part in this paper, the following compounds were prepared: $2CaO.SiO_2$ (largely in the gamma form), $3CaO.SiO_2$, $K_2O.CaO.SiO_2$, $K_2O.Al_2O_3$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$. The exact compositions were determined by chemical analyses and microscopical examinations. Various mixtures of these compounds were intimately ground in an agate mortar and then heated in open platinum boats in an electric furnace at about 1,250° C for

[1] Figures in brackets indicate the literature references at the end of this paper.

½ hour. Losses of potash by volatilization from these preparations were determined by weight differences before and after heating, and compensating additions of K_2O were made. The heated preparations were reground and placed in sealed bottles, which were shaken to insure a high degree of homogeneity. Small charges for thermal study were taken from these base samples, the general procedure, previously outlined [1, 2], being followed.

Charges were examined microscopically by two different methods—powder specimens viewed by transmitted light, and polished thin sections which were viewed by both transmitted and reflected light.

III. PHASE EQUILIBRIA

1. THE SYSTEM $2CaO.SiO_2$-$K_2O.CaO.SiO_2$

Mixtures of $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ throughout the entire range were studied. The compound $K_2O.CaO.SiO_2$ persisted in the completely crystallized charges until the $2CaO.SiO_2$:$K_2O.CaO.SiO_2$ ratio of 9:1 was reached. In this charge only one phase, with the exception of about 0.5 percent of extraneous material, existed. The amounts of this phase had been increasing with increasing ratios of $2CaO.SiO_2$ to $K_2O.CaO.SiO_2$ in this series of changes. The ratio of 9:1 by weight, corresponding to a molar ratio of 11:1, indicated that 11 molecules of $2CaO.SiO_2$ combined with 1 molecule of $K_2O.CaO.SiO_2$ to form a new compound $K_2O.23CaO.12SiO_2$ containing 4.48 percent of K_2O, 61.28 percent of CaO, and 34.25 percent of SiO_2. The X-ray diffraction pattern[2] obtained from this charge, while not very sharp, differed distinctly from the pattern of β-$2CaO.SiO_2$ and $K_2O.CaO.SiO_2$. Although the evidence points to the probable existence of the compound $K_2O.23CaO.12SiO_2$, it is recognized that points on a liquidus curve near $K_2O.23CaO.12SiO_2$ would be necessary to establish the composition. The possibility of limited solid solution of $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ with a compound having a composition slightly different from $K_2O.23CaO.12SiO_2$ remains. The temperatures which would be required for the location of the liquidus curve in this portion of the system are far beyond the limits of the furnace employed.

McMurdie [4], working independently, also came to the conclusion that a ternary compound having the composition $K_2O.23CaO.12SiO_2$ probably exists in the K_2O-CaO-SiO_2 system.

The thermal data for the system are given in table 1. It will be seen from the table that no glass was found in any of the quenched samples containing more than 90 percent of $2CaO.SiO_2$ and that the charges apparently were composed of only one phase in each case. The refractive indices of these charges increased as the ratio of $2CaO.SiO_2$:$K_2O.CaO.SiO_2$ increased, and it became increasingly difficult to distinguish the material from β-$2CaO.SiO_2$. Polysynthetic twinning, characteristic of β-$2CaO.SiO_2$ which had at some time been in the α state, was common. These results indicated the possibility that the compound $K_2O.23CaO.12SiO_2$ passed into solid solution with β-$2CaO.SiO_2$ in all proportions. The X-ray diffraction pattern obtained from the charge composed of 91.4 percent of β-$2CaO.SiO_2$ and 8.6 percent of $K_2O.23CaO.12SiO_2$, however, showed the lines characteristic of β-$2CaO.SiO_2$ as well as those characteristic

[2] All X-ray photographs referred to in this paper were made by H. F. McMurdie.

of $K_2O.23CaO.12SiO_2$. The lines of the latter compound were considerably weaker than those in the X-ray photograph of the charge composed of 90 percent of $2CaO.SiO_2$ and 10 percent of $K_2O.CaO.SiO_2$. Since the X-ray data ruled out the possibility of continuous solid solution, it was assumed that intimate crystallization of the two compounds had occurred, and because of the similarity in optical properties, the product appeared as one phase. This was all the more likely since no liquid was formed in any case from which one of the phases could crystallize. The complexity of the twinning also was a factor in rendering identification more difficult.

TABLE 1.—*Thermal data relative to the system* $2CaO.SiO_2$-$K_2O.CaO.SiO_2$

Note: In this and in subsequent tables the following abbreviations apply:

C_2S	for $2CaO.SiO_2$	Tables 1 and 4
KCS	for $K_2O.CaO.SiO_2$	
$KC_{23}S_{12}$	for $K_2O.23CaO.12SiO_2$	
C_3S	for $3CaO.SiO_2$	Table 5
C_3A	for $3CaO.Al_2O_3$	
C_4AF	for $4CaO.Al_2O_3.Fe_2O_3$	

Composition		Temperature of quench	Examination
C_2S	KCS		
%	%	°C	
0	100	1,625	Glass; small amount of crystalline material.
		1,617	All crystalline. (mp.1,630° C, according to Morey, Kracek, and Bowen.
5	95	1,627	Glass.
		1,619	KCS; glass.
		1,594	KCS: $KC_{23}S_{12}$; trace of glass.
8	92	1,598	Glass.
		1,590	$KC_{23}S_{12}$; KCS.
10	90	1,650	Glass.
		1,637	Do.
		1,625	Small amount of $KC_{23}S_{12}$; glass.
		1,598	$KC_{23}S_{12}$; KCS; glass.
15	85	1,670	Glass.
		1,660	Small amount of $KC_{23}S_{12}$; much glass.
		1,600	$KC_{23}S_{12}$; glass.
		1,590	$KC_{23}S_{12}$; KCS.
20	80	1,660	$KC_{23}S_{12}$; glass.
		1,598	$KC_{23}S_{12}$; KCS; slight amount of glass.
		1,590	$KC_{23}S_{12}$; KCS.
30	70	1,650	$KC_{23}S_{12}$; glass.
		1,618	Do.
		1,640	Do.
40	60	1,612	Do.
		1,598	$KC_{23}S_{12}$; KCS; slight amount of glass.
		1,590	$KC_{23}S_{12}$; KCS.
50	50	1,640	$KC_{23}S_{12}$; glass.
		1,600	Do.
		1,590	$KC_{23}S_{12}$, KCS; trace of glass.
		1,580	$KC_{23}S_{12}$; KCS.
85	15	1,660	$KC_{23}S_{12}$; glass.
		1,600	Do.
		1,590	$KC_{23}S_{12}$; KCS.
		1,520	$KC_{23}S_{12}$; about 7% of KCS.
88	12	1,660	$KC_{23}S_{12}$; glass.
		1,520	$KC_{23}S_{12}$; about 2% of KCS.
90	10	1,650	Except for trace of glass, one crystalline phase.
		1,600	One crystalline phase.
		1,520	Do.
91.4	8.6	1,628	Apparently one crystalline phase.
		1,520	Do.
95	5	1,628	Do.
		1,555	Do.
98	2	1,628	Do.
		1,555	Do.
100	0	----------	(mp. 2,130° C, according to Rankin and Wright).

None of the charges which contained more than 15 percent of $2CaO.SiO_2$ was melted completely at the temperatures employed (see table 1). Sufficient data were obtained, however, to indicate that $2CaO.SiO_2$ and $K_2O.CaO.SiO_2$ constitute a binary system containing one intermediate compound having the probable composition $K_2O.23CaO.12SiO_2$. The composition of the eutectic formed by $K_2O.23CaO.12SiO_2$ and $K_2O.CaO.SiO_2$ was 8.9 percent of the former, 91.1 percent of the latter (8.0 percent of $2CaO.SiO_2$ and 92.0 percent of $K_2O.CaO.SiO_2$). The eutectic melted at 1,598°±10° C. The liquidus temperature of the charge containing 15 percent of $2CaO.SiO_2$ and 85 percent of $K_2O.CaO.SiO_2$ was 1,670° C. This temperature

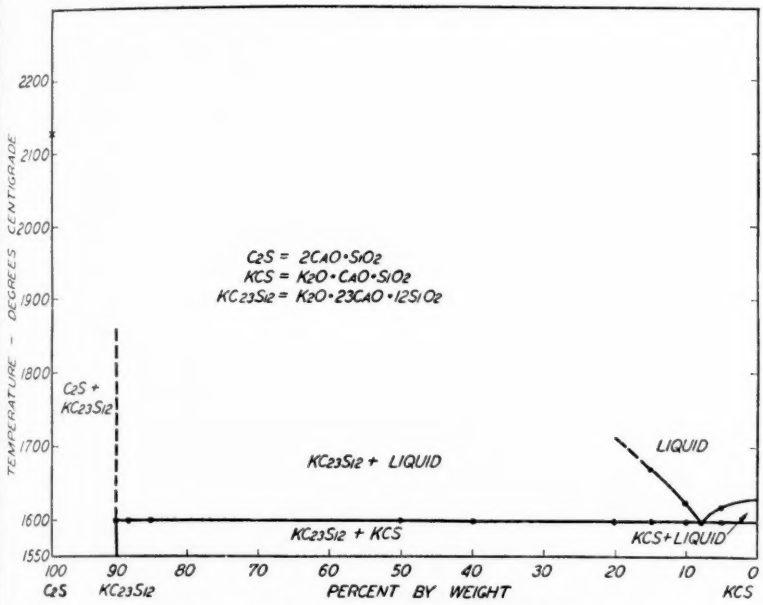

FIGURE 1.—*The system* $2CaO.SiO_2$-$K_2O.CaO.SiO_2$.

was about the maximum obtainable in the furnace employed; hence the thermal data obtained for the system were incomplete beyond this point. The incomplete temperature-concentration diagram is given in figure 1.

A much larger quantity of the compound $K_2O.23CaO.12SiO_2$ was prepared in a horizontal electric furnace [5]. In order to overcome the difficulties of adjusting the K_2O content of the preparation, caused by the increase in volatilization of K_2O during repeated heat treatments in open platinum boats, the following procedure was adopted, after many preliminary tests. To the powdered $CaCO_3$, $K_2O.SiO_2$ and SiO_2, mixed in the proportions $K_2O.23CaO.12SiO_2$, there was added a weighed quantity of potassium oxalate equal in K_2O content to that previously introduced as $K_2O.SiO_2$. Thus the total K_2O content of the unheated mixture was twice that required. The K_2O content of the heated preparation was determined directly by chemical analysis, and not by loss of weight. The mixture was subjected

to a preliminary heat treatment of 1,250° C for 8 minutes and then finely ground. Three successive heat treatments at 1,500° C for 8 minutes were made with intermediate fine grinding, microscopical examination, and complete chemical analysis. The final product consisted almost entirely of a single crystalline phase, apparently identical with that found in the small heated charge of a 9:1 $2CaO.SiO_2$:K_2O. $CaO.SiO_2$ mixture. In addition to this crystalline phase, a microscopical examination showed the presence of small quantities of extraneous materials. They consisted of a few grains of CaO, occasional thin veins of an isotropic material having a low index of refraction, and a number of small specks of an unidentifiable substance.

A comparison of the chemical analysis of the preparation with the theoretical composition of $K_2O.23CaO.12SiO_2$ is given in table 2.

TABLE 2.—*A comparison of the chemical analysis of a preparation of* $K_2O.23CaO.12SiO_2$ *with the theoretical composition*

Constituent	Preparation [1]	Theoretical $K_2O.23CaO.12SiO_2$
	%	%
CaO	61.51	61.28
SiO_2	33.55	34.25
K_2O	4.60	4.48
R_2O_3	.38	
Free CaO	.4	

[1] Chemical analysis by E. G. Siggers. Potash was determined by the J. Lawrence Smith procedure.

The amounts of SiO_2 and of combined CaO (61.11 percent) are slightly less than their respective theoretical values, but that of K_2O is slightly more. The presence of the extraneous material mentioned may have been the result of the slight deficiency of SiO_2 and CaO, the excess of K_2O, and the presence of the small amounts of R_2O_3.

A microscopical examination of a powdered sample of this preparation showed that $K_2O.23CaO.12SiO_2$ was present as irregularly shaped, somewhat rounded grains, exhibiting complex polysynthetic twinning similar to that of α-$2CaO.SiO_2$ but having lower refractive indices and birefringence than that compound.

A comparison of the optical properties of $K_2O.23CaO.12SiO_2$ with those of α- and β-$2CaO.SiO_2$ and of $3CaO.SiO_2$ is given in table 3.

TABLE 3.—*Optical properties of* $K_2O.23CaO.12SiO_2$, α- *and* β-$CaO.SiO_2$, *and* $3CaO.SiO_2$

Compound	Optical character	Index of refraction		
		α	γ	Double refraction
$K_2O.23CaO.12SiO_2$	Uniaxial positive	1.695	1.703	0.008
α-$2CaO.SiO_2$	Biaxial positive	1.715	1.737	.022
β-$2CaO.SiO_2$	do	1.717	1.735	.018
$3CaO.SiO_2$	do	Mean=1.715		.005

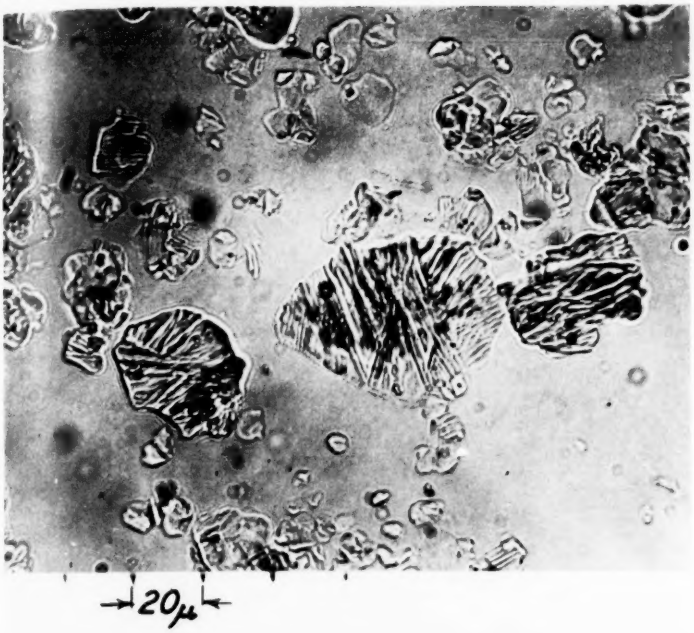

FIGURE 2.—*Crystals having the probable formula* $K_2O.23CaO.12SiO_2$.
Ordinary transmitted light.

FIGURE 3.—*Crystals having the probable formula* $K_2O.23CaO.12SiO_2$.
Same field as figure 2 but between crossed nicols.

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It was not possible to measure accurately the refractive indices of most of the grains of $K_2O.23CaO.12SiO_2$ because of the complex twinning, accordingly the values given in the above table were obtained from grains less complexly twinned.

Figure 2 is a photomicrograph of a powder sample of this preparation in transmitted ordinary light. Figure 3 shows the same field between crossed nicols.

A comparison, given in table 4, of the interplanar spacings of the X-ray diffraction pattern obtained from a powdered sample of this preparation, with that of β-$2CaO.SiO_2$, shows the absence of most of the lines characteristic of β-$2CaO.SiO_2$, and the presence of 10 lines not found in the pattern of β-$2CaO.SiO_2$. The differences between the patterns of $3CaO.SiO_2$ [6] and $K_2O.23CaO.12SiO_2$ are even more marked.

TABLE 4.—*Interplanar spacings of the diffraction patterns of* β-$2CaO.SiO_2$ and $K_2O.23CaO.12SiO_2$

[Measured by H. F. McMurdie]

[s=strong, vs=very strong, m=medium, w=weak, vw=very weak, b=broad.]

β-$2CaO.SiO_2$		$K_2O.23CaO.12SiO_2$		β-$2CaO.SiO_2$		$K_2O.23CaO.12SiO_2$	
D_{hkl}	Estimated relative intensity	D_{hkl}	Estimated relative intensity	D_{hkl}	Estimated relative intensity	D_{hkl}	Estimated relative intensity
A		*A*		*A*		*A*	
3.97	w [1]			1.902	w		
3.35	w			1.846	vw		
3.06	w			1.802	w-b	1.805	w
2.88	w					1.789	w
2.79	vs			1.726	vw		
2.73	vs	2.75	vs-b			1.717	w
2.66	vw	2.63	w	1.708	w		
2.606	m			1.690	vw		
2.556	vw			1.665	vw		
2.460	w			1.635	m		
2.410	w					1.632	vw
2.291	w	2.29	w	1.613	m		
		2.240	w			1.593	m
2.217	vw			1.590	w		
2.195	s			1.576	w		
		2.185	m	1.553	w		
2.159	vw			1.528	w		
2.130	vw			1.486	w	1.484	vw
2.083	vw			1.451	vw		
2.048	w			1.429	vw		
		2.034	m	1.420	vw		
2.017	w					1.417	vw
1.984	m			1.398	w		
		1.959	s	1.373	m		
1.924	vw					1.370	w-b

IV. STATE OF COMBINATION OF K_2O IN PORTLAND CEMENT CLINKER

1. REACTIONS OF K_2O IN MIXTURES CONTAINING COMPOUNDS PRESENT IN PORTLAND CEMENT CLINKER

As was stated in the introduction to this paper, it has been established that $K_2O.Al_2O_3$ is the only stable compound of K_2O in that part of the K_2O-CaO-Al_2O_3 system which is of interest in the study of portland cement clinker.

As a further step in the determination of the state of combination of K_2O in clinker, it is important to discover whether $K_2O.Al_2O_3$ or some other compound containing K_2O is stable in that part of the five-component system, K_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2, related to cement clinker composition.

2. RELATIONS OF $3CaO.SiO_2$ AND $K_2O.Al_2O_3$

For the preliminary work on this problem, mixtures within the range of 99 percent of $3CaO.SiO_2$, 1 percent of $K_2O.Al_2O_3$ to 85 percent of $3CaO.SiO_2$, 15 percent of $K_2O.Al_2O_3$ were prepared. Because it was observed that liquid was first formed in the charges at some temperature between 1,400° and 1,450° C, the samples were heated at 1,450° C for 10 minutes, cooled to 1,400° C at the rate of ½° C per minute, and then quenched. The compound $K_2O.Al_2O_3$, which is formed in the K_2O-CaO-Al_2O_3 system, was not positively identified in any of the completely crystallized charges in which the molar ratio of $3CaO.SiO_2$ to $K_2O.Al_2O_3$ was greater than 6:1 (87.5 percent of $3CaO.SiO_2$ and 12.5 percent of $K_2O.Al_2O_3$). Large amounts of a birefringent phase with a mean index of about 1.70 were observed. Tricalcium aluminate and much uncombined CaO were present also. Tricalcium silicate was identified only in charges resulting from mixtures originally containing 95 percent or more of $3CaO.SiO_2$. The amounts were small and probably represented the excess of $3CaO.SiO_2$ in the reaction with $K_2O.Al_2O_3$. In mixtures having the molar ratio $3CaO.SiO_2$:$K_2O.Al_2O_3$ of 6:1 or less, the amounts of the new crystalline phase appeared to be about the same as in mixtures of higher ratios, but some residual $K_2O.Al_2O_3$ was apparently present in addition to $3CaO.Al_2O_3$ and CaO. Assuming that the new crystalline phase which is the product of these reactions has the composition $K_2O.23CaO.12SiO_2$, the following equation expresses the reaction occurring when the 12:1 ratio mixture (93 percent of $3CaO.SiO_2$ and 7 percent of $K_2O.Al_2O_3$) was heated:

$$12\ (3CaO.SiO_2) + K_2O.Al_2O_3 \rightarrow K_2O.23CaO.12SiO_2 + 3CaO.Al_2O_3 + 10CaO$$

In mixtures having $3CaO.SiO_2$:$K_2O.Al_2O_3$ ratios less than 12:1, there is an excess of $K_2O.Al_2O_3$ present, but this may not always be identified in the heated charges because of the relatively small percentage of this compound associated with the reaction products. Thus, in the charge resulting from the heating of a mixture having a 6:1 ratio, the weight of the $K_2O.Al_2O_3$ calculated to be present is only 6.3 percent of the total. The distribution of this amount of $K_2O.Al_2O_3$ as interstitial material throughout the specimen would render identification difficult.

3. RELATIONS OF $2CaO.SiO_2$ AND $K_2O.Al_2O_3$

Base mixtures of $2CaO.SiO_2$ and $K_2O.Al_2O_3$ within the range of molar ratios of $2CaO.SiO_2$ to $K_2O.Al_2O_3$ of 1:1 to 10:1, respectively, were prepared and given the same thermal treatment as was given the mixtures of $3CaO.SiO_2$ and $K_2O.Al_2O_3$. Microscopical examinations indicated that the new crystalline phase, found as a product of the reactions between $3CaO.SiO_2$ and $K_2O.Al_2O_3$, was formed in the $2CaO.SiO_2$-$K_2O.Al_2O_3$ reactions also. No $3CaO.Al_2O_3$ or free CaO was observed but some $K_2O.Al_2O_3$ was identified in charges having a low $2CaO.SiO_2$:

$K_2O.Al_2O_3$ ratio. As the ratio of $2CaO.SiO_2$:$K_2O.Al_2O_3$ increased, the amount of new crystalline phase increased until a ratio of about 6:1 or 7:1 was reached, charges of these ratios appearing to consist largely of the new crystalline product together with an apparently crystalline but unidentifiable material with low refractive index occurring as veinlets. Again assuming that $K_2O.23CaO.12SiO_2$ is a product of these reactions, it is likely that $CaO.Al_2O_3$ and some residual $K_2O.Al_2O_3$ existed in the charges as the thin veins of unidentified material to which reference has been made.

4. RELATIONS OF $3CaO.SiO_2$, $2CaO.SiO_2$, AND $K_2O.Al_2O_3$

Since it was found that CaO and $3CaO.Al_2O_3$ were two of the products of reaction of $3CaO.SiO_2$ and $K_2O.Al_2O_3$ and that neither was identified in the reaction products of $2CaO.SiO_2$ and $K_2O.Al_2O_3$, it is reasonable to expect that at some definite proportion of the two calcium silicates and $K_2O.Al_2O_3$ the amount of CaO derived from the silicates will be just equal to the amount required by the Al_2O_3 to form $3CaO.Al_2O_3$. Accordingly, in the preliminary work, various mixtures of the two silicates with $K_2O.Al_2O_3$ were studied. As a typical case, it was found that a completely crystallized sample, resulting from a mixture corresponding to 2 molecules of $3CaO.SiO_2$, 4 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O.Al_2O_3$, contained the same principal phase observed before, a few grains of $3CaO.Al_2O_3$, a small amount of uncombined CaO, and some residual $K_2O.Al_2O_3$. The exact proportions were not attained, however, until after the discovery of the compound $K_2O.23CaO.12SiO_2$ in the $2CaO.SiO_2$-$K_2O.CaO.SiC_2$ system. A charge consisting of the equivalent of 2 molecules of $3CaO.SiO_2$, 10 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O.Al_2O_3$ was prepared, and after heat treatment, examined by both the powder and polished thin-sections methods. It appeared to consist of two phases only, the more abundant phase being the new crystalline compound and the less abundant phase being $3CaO.Al_2O_3$. The mean index of refraction of the major phase was about 1.70 and the birefringence about 0.01. This reaction may be expressed as

$$2(3CaO.SiO_2)+10(2CaO.SiO_2)+K_2O.Al_2O_3 \rightarrow K_2O.23CaO.12SiO_2+3CaO.Al_2O_3.$$

The results of these tests indicate the probable formation of $K_2O.23CaO.12SiO_2$ in completely crystallized preparations having compositions in the K_2O-CaO-Al_2O_3-SiO_2 system pertinent to those of portland cement clinker.

5. RELATIONS OF $3CaO.SiO_2$, $2CaO.SiO_2$, $K_2O.Al_2O_3$, AND Fe_2O_3

It has been indicated in this report that the compound $K_2O.23Ca$-$O.12SiO_2$ can exist in laboratory clinker containing the oxides K_2O, CaO, Al_2O_3, and SiO_2 in amounts likely to be found in portland cement clinker. In addition to these oxides, Fe_2O_3 is present in the commercial product. Accordingly an additional mixture was prepared including this other principal oxide, Fe_2O_3. This mixture, represented by

$$3(3CaO.SiO_2)+9(2CaO.SiO_2)+K_2O.Al_2O_3+Fe_2O_3,$$

was heated to 1,400° C and cooled to 1,295° C at a rate of 2.5° C per minute. The completely crystallized product apparently consisted of only two phases—probably $K_2O.23CaO.12SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$.

The maximum and minimum refractive indices, 1.722 and 1.713, of the potash compound in this charge are considerably higher than those of $K_2O.23CaO.12SiO_2$ in iron-free charges, possibly because of limited solid solution with an iron compound. Although this increase in indices makes difficult the distinction of the potash compound from $3CaO.SiO_2$ and β-$2CaO.SiO_2$, the maximum index of refraction of the iron-bearing $K_2O.23CaO.12SiO_2$ is lower than that of β-$2CaO.SiO_2$ (1.735) and the double refraction (.009) is somewhat higher than that of pure $3CaO.SiO_2$ (.005).

Another charge was prepared by adding 25 percent of $4CaO.Al_2O_3.Fe_2O_3$ to the mixture represented by 2 molecules of $3CaO.SiO_2$, 10 molecules of $2CaO.SiO_2$, and 1 molecule of $K_2O.Al_2O_3$, and the resulting mixture was heated to 1,550° C and cooled slowly to 1,260° C. The product appeared to consist of $K_2O.23CaO.12SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$ only. Thus, in these studies, there has been no indication that any compound of potash other than $K_2O.23CaO.12SiO_2$ exists under equilibrium conditions in portland cement clinker insofar as the major oxide constituents are concerned.

These results explain data obtained in a previous unpublished investigation, conducted by the author in 1929. It was observed that greater difficulty was experienced in obtaining complete combination of the CaO with the other oxide constituents of laboratory clinker mixtures during calcination when K_2O was substituted for like percentages of CaO, that is to say, the amounts of free CaO in the clinkers after calcination at a definite temperature for a definite time increased with increasing amounts of substituted K_2O. These results are shown in table 5. The oxide compositions of the raw mixtures calculated to the clinker basis and the oxide compositions of the clinkers assuming a loss of 30 percent of the potash on heating are given. The assumption is based on the amounts of K_2O which were lost from five representative charges analyzed after heating in the open platinum boats, as also indicated in table 5. The potential compound compositions, considering the K_2O combined as $K_2O.23CaO.12SiO_2$, have been calculated and are given in table 5. The reasons for the increased difficulty in obtaining complete combination of the CaO with the other oxides, as shown by increased amounts of uncombined CaO remaining in the clinkers, become apparent after a consideration of the changes in the ultimate compositions resulting from the introduction of K_2O. The substitution of K_2O for CaO resulted in greatly increased $3CaO.SiO_2$-$2CaO.SiO_2$ ratios because of the formation of $K_2O.23CaO.12SiO_2$. In three cases no $2CaO.SiO_2$ was present and CaO was an equilibrium product (Nos. 12, 15, 16). The formation of $2CaO.SiO_2$ is very rapid at temperatures of 1,400° C and above. Tricalcium silicate, for the most part, results from the reaction $2CaO.SiO_2+CaO \rightarrow 3CaO.SiO_2$; but this reaction becomes more and more sluggish as the amount of $2CaO.SiO_2$ decreases, and equilibrium is attained with greater difficulty. The existence of the compound $K_2O.23CaO.12SiO_2$ explains why, for example, the introduction of 2.1 percent of K_2O into a mixture caused an increase in the amount of uncombined CaO, from 0.1 to 7.9 percent remaining after calcination of 1,525° C, even though the total CaO had been decreased from 68.8 to 66.4 percent (Nos. 13 and 16).

TABLE 5.—*Effect of the substitution of* K_2O *for* CaO *on the combination of* CaO *in laboratory cement mixtures*

Mixture No.	Oxide composition of raw mixture (clinker basis)					Oxide composition based on 30-percent loss of K_2O during heating [a]					Potential compound composition						Uncombined CaO after being heated at—			
	CaO	Al_2O_3	Fe_2O_3	SiO_2	K_2O	CaO	Al_2O_3	Fe_2O_3	SiO_2	K_2O	C_3S	C_2S	$KCaSi_2$	C_3A	C_4AF	CaO	1,400° C	1,450° C	1,500° C	1,525° C
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	66.0	11.0	0	23.0	0	66.0	11.0	0	23.0	0	19.5	51.3	0	29.2	0	0	....	0.7	0.0	0.0
2	65.0	11.0	0	23.0	1	65.20	11.03	0	23.07	0.7	17.3	37.8	15.7	29.2	0	0	....	.2	.1	....
3	64.0	11.0	0	23.0	2	64.39	11.07	0	23.14	1.4	15.0	24.4	31.3	29.3	0	0	....	3.5	2.6	....
4	63.0	11.0	0	23.0	3	63.57	11.10	0	23.21	2.1	13.0	10.6	47.0	29.4	0	0	....	5.3	2.8	2.6
5	67.0	10.0	0	23.0	0	67.0	10.0	0	23.0	0	30.5	43.0	0	26.5	0	0	7.7	1.8	0.3	0.0
6	66.0	10.0	0	23.0	1	66.20	10.03	0	23.07	0.7	28.2	29.6	15.7	26.6	0	0	6.7	0.7	.5	....
7	65.0	10.0	0	23.0	2	65.39	10.06	0	23.14	1.4	25.8	16.2	31.3	26.7	0	0	7.4	5.4	4.5	3.1
8	64.0	10.0	0	23.0	3	64.58	10.09	0	23.21	2.1	23.3	3.0	47.0	26.7	0	0	8.0	7.5	7.0	4.3
9	67.0	7.5	2.5	23.0	0	67.0	7.5	2.5	23.0	0	44.0	32.8	0	15.6	7.6	0	2.0	1.1	0.4	0.0
10	66.0	7.5	2.5	23.0	1	66.20	7.52	2.51	23.07	0.7	41.5	19.6	15.7	15.7	7.6	0	2.0	1.6	.9	.7
11	65.0	7.5	2.5	23.0	2	65.39	7.54	2.52	23.14	1.4	39.2	6.1	31.3	15.7	7.7	0	6.2	4.3	3.7	3.6
12	64.0	7.5	2.5	23.0	3	64.58	7.56	2.53	23.21	2.1	27.2	0	47.0	15.7	7.7	2.4	9.7	7.3	6.9	6.8
13	68.8	9.0	0	22.2	0	68.8	9.0	0	22.2	0	50.7	25.5	0	23.9	0	0	....	3.4	2.3	0.1
14	67.8	9.0	0	22.2	1	68.0	9.03	0	22.27	0.7	48.2	12.3	15.7	23.9	0	0	....	1.9	1.0	.5
15	66.8	9.0	0	22.2	2	67.20	9.06	0	22.34	1.4	44.2	0	31.3	24.0	0	0.4	....	6.6	5.4	3.5
16	65.8	9.0	0	22.2	3	66.40	9.08	0	22.40	2.1	24.1	0	47.0	24.1	0	4.8	....	9.8	8.4	7.9

[a] Amounts of K_2O volatilized in 5 representative clinkers are as follows:

Mix No.	Original K_2O	K_2O in clinker calcined at indicated temperature		Percentage loss of K_2O
	%	%	° C	%
1	1.0	0.75	1,450°	25
4	3.0	1.96	1,500°	35
8	3.0	1.87	1,500°	38
12	3.0	2.15	1,500°	28
15	2.0	1.52	1,450°	24

As shown in table 5, the addition of small amounts of K_2O to clinker mixtures causes marked changes in the relative amounts of the calcium silicates. Thus, for example, 1 percent of K_2O may react with 21.9 percent of $2CaO.SiO_2$ to form 22.3 percent of $K_2O.23CaO.12SiO_2$ with the liberation of 0.6 percent of CaO. This 0.6 percent of CaO in turn combines with 1.9 percent of additional $2CaO.SiO_2$ to form 2.5 percent of $3CaO.SiO_2$, 23.8 percent of $2CaO.SiO_2$ having been removed from the mixture by the introduction of 1 percent of K_2O. In a mixture in which the potential $2CaO.SiO_2$ is less than 23.8 percent, the remaining K_2O reacts with the $3CaO.SiO_2$ to form $K_2O.23CaO.12SiO_2$ and CaO. Under these conditions free CaO is present as an equilibrium product; 1 percent of K_2O reacting with 29.1 percent of $3CaO.SiO_2$ to liberate 7.7 percent of CaO.

Inspection of the amounts of K_2O and of free CaO in certain analyzed commercial clinkers employed in other investigations by this laboratory, however, revealed a few cases in which the determined free CaO was less than that calculated, assuming all of the K_2O combined as $K_2O.23CaO.12SiO_2$. This has suggested that some of the K_2O may have reacted with the minor acidic constituents of these clinkers and reduced the amount of potash available for the formation

of $K_2O.23CaO.12SiO_2$, the final result being a reduction in the amount of free CaO in the clinker. For example, if all of the SO_3 in a clinker containing 0.2 percent of SO_3 reacted with K_2O, the amount of the latter combined as K_2SO_4 would be about 0.24 percent. The reaction of this quantity of K_2O with SO_3 rather than with CaO and SiO_2 would decrease the amount of free lime in the clinker by about 1.8 percent.

Additional studies of systems involving potash and minor constituents of clinker are now in progress, and there are indications that such materials may produce marked effects on the constitution of clinker. Evidence that $K_2O.23CaO.12SiO_2$ reacts with $CaSO_4$ to form $2CaO.SiO_2$ and K_2SO_4 has been obtained. Recent microscopical examinations of commercial clinkers have revealed the presence of K_2SO_4 in many cases.

In this laboratory the compound $K_2O.23CaO.12SiO_2$ has not as yet been identified definitely in commercial clinkers by means of microscopical examinations. This may have been due to (1) lack of equilibrium during cooling of the clinker resulting in the formation of an unstable compound or of glass containing potash, (2) the reaction of most of the potash present with minor acidic oxides, such as SO_3, (3) mistaken identification in powdered specimens due to the similarity in the indices of refraction to those of the calcium silicates, (4) mistaken identification due to the similarity of the etching characteristics of the potash compound with those of one or the other, or both, of the calcium silicates.

V. SUMMARY

A portion of the system $2CaO.SiO_2$-$K_2O.CaO.SiO_2$ has been investigated by the phase-equilibrium method and the results are presented. A temperature-concentration diagram for the binary system, incomplete because of the temperature limitations of the furnace employed, has been constructed.

One intermediate compound was found in the system, having the composition $K_2O.23CaO.12SiO_2$. The reported optical properties and the interplanar spacings of the X-ray diffraction pattern were determined on a preparation having the composition closely approaching that of the theoretical for $K_2O.23CaO.12SiO_2$.

The results of studies on mixtures of $3CaO.SiO_2$ and $K_2O.Al_2O_3$, and of $2CaO.SiO_2$ and $K_2O.Al_2O_3$, indicate that the compound $K_2O.Al_2O_3$, which previously had been shown to be stable in the K_2O-CaO-Al_2O_3 and in the K_2O-CaO-Al_2O_3-Fe_2O_3 systems does not exist in the region of the K_2O-CaO-Al_2O_3-SiO_2 system, which is directly concerned with portland cement. Possibly these results may be explained by the potash combining with CaO and SiO_2 to form the compound K_2O-$.23CaO.12SiO_2$.

The compound $K_2O.23CaO.12SiO_2$ was found to exist in a region of the K_2O-CaO-Al_2O_3-SiO_2-Fe_2O_3 system in which portland cement compositions fall.

While it is recognized that various minor acidic constituents generally existing in commercial portland cement clinker may combine with all or part of the potash present, evidence was obtained that K_2O combines as $K_2O.23CaO.12SiO_2$ in the presence of the major constituents CaO, Al_2O_3, SiO_2, and Fe_2O_3, in the proportions occurring in portland cement, and that this ternary compound will occur in clinker limited to those components prepared under equilibrium conditions of heating and cooling.

The author is indebted to G. W. Ward for his assistance and advice in connection with the microscopical studies.

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A CRITICAL STUDY OF SOME FACTORS AFFECTING THE BREAKING STRENGTH AND ELONGATION OF COTTON YARNS

By Herbert F. Schiefer and Richard S. Cleveland [1]

ABSTRACT

The results of single-strand tests to determine the breaking strength and elongation of cotton yarns varying in yarn number and spun with four twist multipliers are reported. Pendulum and inclined-plane types of testing machines and two rates of loading were used in the tests. The results give information regarding the corrections of these machines, variability of the yarns, and the number of tests required for a given precision and probability. The effect of rate of loading on the breaking strength and elongation is discussed. The tests on the inclined-plane machine yielded a significantly higher breaking strength and lower elongation than the tests on the pendulum machine. These unexpected differences are not attributable to a difference in the rates of loading between the two machines. They are explainable on the basis of the mechanics of the two types of machines.

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I. INTRODUCTION

The results obtained in testing textiles for breaking strength and elongation vary with the type of testing machine used and the rate of loading. Comprehensive and systematic studies of these variations have been rather limited in scope, and the variations continue to present a serious problem in the preparation of textile specifications and in the testing of textiles. The need for further information on the effect of rate of loading on the breaking strength of cotton yarns by Subcommittee B–1, Section II on Machines, of Committee D–13, American Society for Testing Materials, and by others led to the present work.

The tests were planned to yield data which could be treated readily by statistical methods and to cover not only rate of loading and type

[1] Richard S. Cleveland collaborated in this study before he left the National Bureau of Standards in April 1940.

of testing machine but also uniformity of the yarns in order to show the number of tests required for a given precision and probability in the results. Further, the effects of yarn number and twist on the breaking strength and elongation of cotton yarns received attention.

II. TESTING MACHINES AND CALIBRATIONS

Two types of testing machines were used. They are known as type *A* and type *B* in ASTM Designation D 76–39. Type *A* is often referred to as the pendulum-type machine, while type *B* is known as the constant specimen-rate-of-load machine,[2] and is commonly referred to as the "Incline Plane Serigraph."

The tests on the type *A* machine were made with 500- and 2,000-g capacities. The machine was operated at speeds of 5 and 12 inches per minute for the movement of the lower jaws. The speed of 5 inches per minute was obtained by the use of an auxiliary pulley. Under these conditions each yarn was loaded at two rates which differed by a factor of 2 or more.

The tests on the type *B* machine were made with 250-, 500-, 1,000-, and 2,000-g capacities. The 2,000-g capacity was attained by adding an auxiliary weight to the cart. Under these conditions each yarn was loaded at two rates which differed by a factor of 2.

Before the tests were made, the two machines were calibrated. Since published information regarding methods of calibration and of the results obtained are meager, and since those obtained on machine *B* are of special interest, the results are presented in detail.

The type A machine was calibrated according to the methods given in ASTM Designations D76–39 and D179–38, as well as by the swinging-pendulum and by the calibrated-spring methods.

In the method given in D76–39, a weight is suspended freely from the upper jaws and the equilibrium position of the pendulum is determined by disengaging the pawls, bringing the pendulum slightly below its equilibrium position, engaging the pawls, and then releasing the pendulum and allowing it to swing up to the equilibrium position with the pawls engaged. The applied weight minus the indicated load is equal to the correction. This correction is plotted against the indicated load in *A* of figures 1 and 2 for the 500- and 2,000-g capacities, respectively.

In the method given in D 179–38, the weight is lowered by means of the lower jaws until it is suspended freely from the upper jaws and with the pawls of the pendulum engaged. The correction is equal to the applied weight minus the indicated load when the weight is completely suspended and the pendulum has come to rest. This correction is plotted against the indicated load in *B* of figures 1 and 2 for the 500- and 2,000-g capacities, respectively. The calibration for the 500-g capacity was then repeated with the pawls disengaged. The correction is plotted against the indicated load in *B′* of figure 1. The difference between *B* and *B′* is approximately 2 percent of the indicated load and represents the friction due to the dragging of the pawls.

In the swinging-pendulum method the pawls were disengaged, and with a weight suspended from the upper jaws, the pendulum was displaced from its equilibrium position and released to swing freely.

[2] G. B. Haven, *A constant load rate testing machine for textiles*, Proc. Am. Soc. Testing Mtls. 23, pt. 2, 640-654 (1923).

The correction is equal to the applied weight minus the load indicated after the pendulum has come to rest. This correction is plotted against the indicated load in *C* of figure 1 for the 500-g capacity. This correction remained practically constant and equal to −15 g throughout the 500-g load range. The larger numerical value of this correction compared with the corrections obtained by the preceding

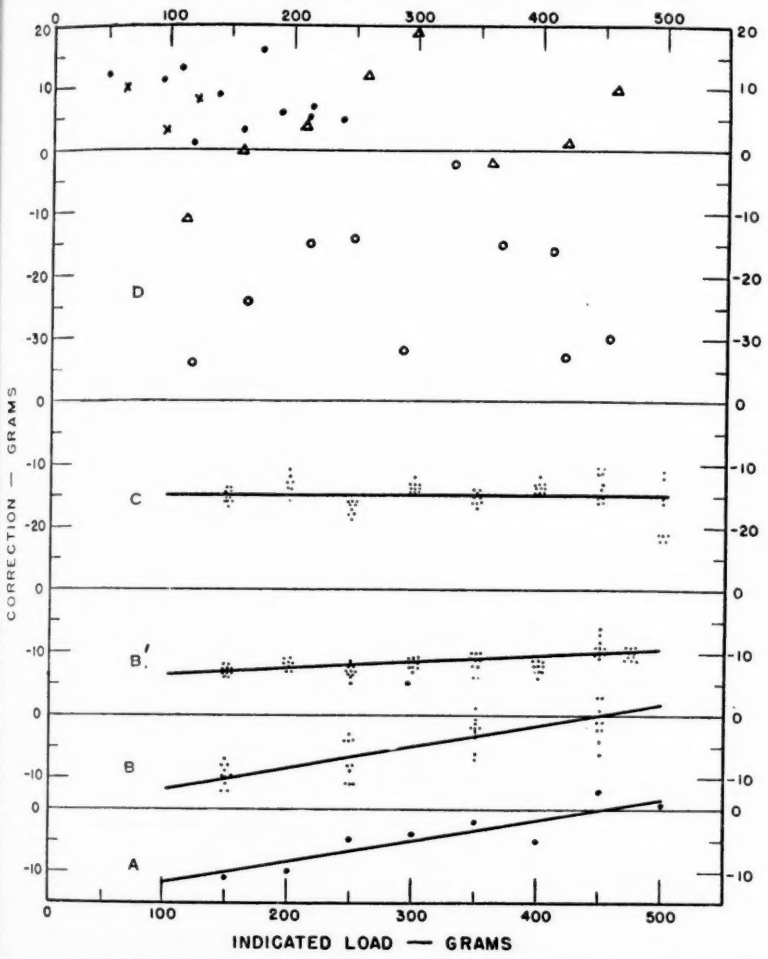

FIGURE 1.—*Calibration correction of the type A machine, 500-g capacity, using different methods of calibration.*

methods is chiefly attributable to the different ways in which the bearing friction of the pendulum and the friction due to the dragging of the pawls enter into the calibration procedure.

In the calibrated-spring method several helical springs which previously had been calibrated with known weights were used. A spring was mounted between the upper and lower jaws of the machine. The lower jaws were lowered by means of the motor, thus elongating

the spring and exerting a pull on the upper jaws and the pendulum. The applied load was ascertained from the elongation of the spring and its calibration plus the weight of the spring. The correction is equal to this applied load minus the indicated load. This correction is plotted in *D* of figures 1 and 2 for the 500- and 2,000-g capacities,

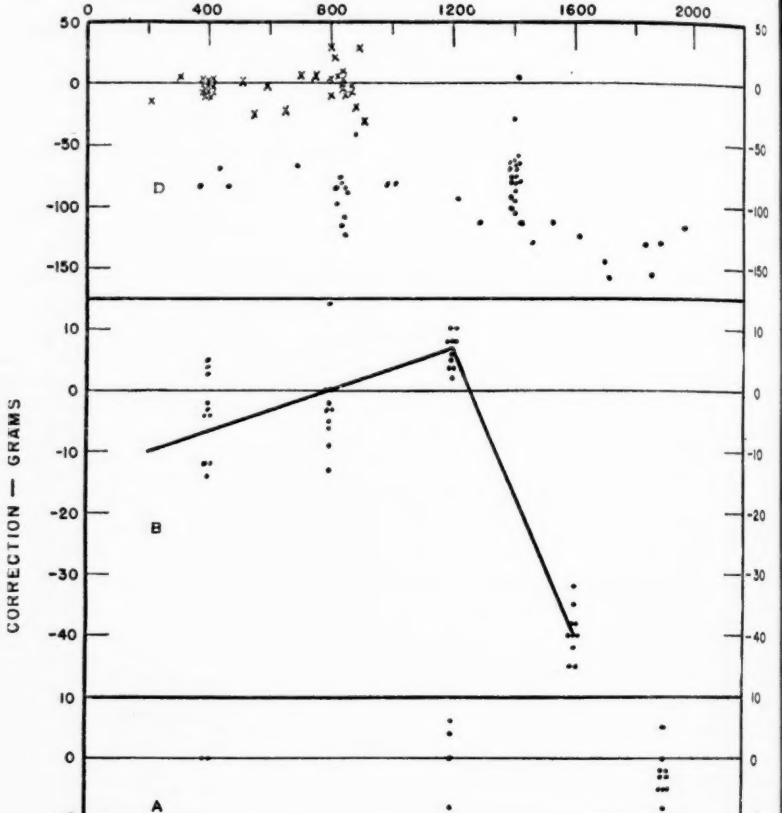

FIGURE 2.—*Calibration correction of the Type A machine, 2,000-g capacity, using different methods of calibration.*

respectively. The different symbols represent the results obtained with different springs. This method gave variable results, the variability being largely due to the inability of ascertaining the correct elongation of the springs. It is not considered a satisfactory method of calibration.

The best corrections to be applied to the test results obtained with this type *A* machine are believed to be those obtained by the two

ASTM calibration procedures. These two methods gave essentially the same values for the 500-g capacity. However, for the 2,000-g capacity the results by both methods were quite variable. The calibration corrections given in table 1, which were applied to the test results in this paper, are based upon the corrections derived from the two ASTM calibration methods.

TABLE 1.—*Calibration corrections for the type A machine*

500-g capacity		2,000-g capacity	
Indicated load	Correction	Indicated load	Correction
g	*g*	*g*	*g*
100	−12	400	−11
150	−10	500	−10
200	−8	600	−9
250	−7	700	−8
300	−5	800	−7
350	−4	900	−6
400	−2	1,000	−5
450	0	1,100	−4
500	+2	1,200	−3

The type *B* machine was calibrated by the weight and pulley method.[3] In this method a weight is fastened to one end of a string which passes over a pulley and has its other end fastened to the cart of the machine. The plane is inclined to a known angle and the weight is adjusted to such an amount that, when started, the cart would proceed down the plane with approximately uniform velocity. The weight corrected for pulley friction is taken as the applied load. The indicated load is the value which the machine records on the chart, namely, the chart ordinate of a uniform scale in inches. The applied load minus the indicated load is equal to the correction.

The correction for each individual calibration is plotted in figure 3 against the indicated load and chart ordinate. The straight line drawn for each capacity indicates zero correction at an indicated load equal to one-half of each capacity and a correction of minus and plus 2 percent of the full capacity at indicated loads equal to zero and full load, respectively. These straight lines represent the calibration data quite well. The deviations of the individual points from these lines probably are due largely to variations in the individual calibration determinations and to variations in the friction of the cart bearings.

The fact that straight lines, having the same percentage correction for each capacity, constitute a good fit of the data suggests that the source of the correction is common to the four capacities. A careful search was made and it was found that the source of this correction resided in the mechanism which moves the recording chart. A schematic drawing of this mechanism is shown in figure 4, where *P* represents the inclined plane. To it are fastened two pulleys, *A* and *B*, which may rotate. A cord, *C*, of length *l*, is fastened at one end to the table at *D*, passes over pulley *B*, and is fastened at the other end to pulley *A* at *E*. The movement of the chart is directly proportional to the angular motion of pulley *A*. The weight of the chart exerts a

[3] R. S. Cleveland, *Calibration of a "constant rate of loading" machine for testing the tensile properties of textiles*, Rayon Textile Monthly **18**, 179–180, 230–232 (March and April 1937).

torque on pulley A and thereby places a tension on cord C. As the inclination of the plane is increased, by lowering the rack, R, at a constant speed, using a motor and reduction gear, the distance from D to B is decreased, and pulley A will rotate enough to take up the slack produced in the cord by the decrease in the distance from D to B. Although the change in the angle of inclination, θ, is such that the

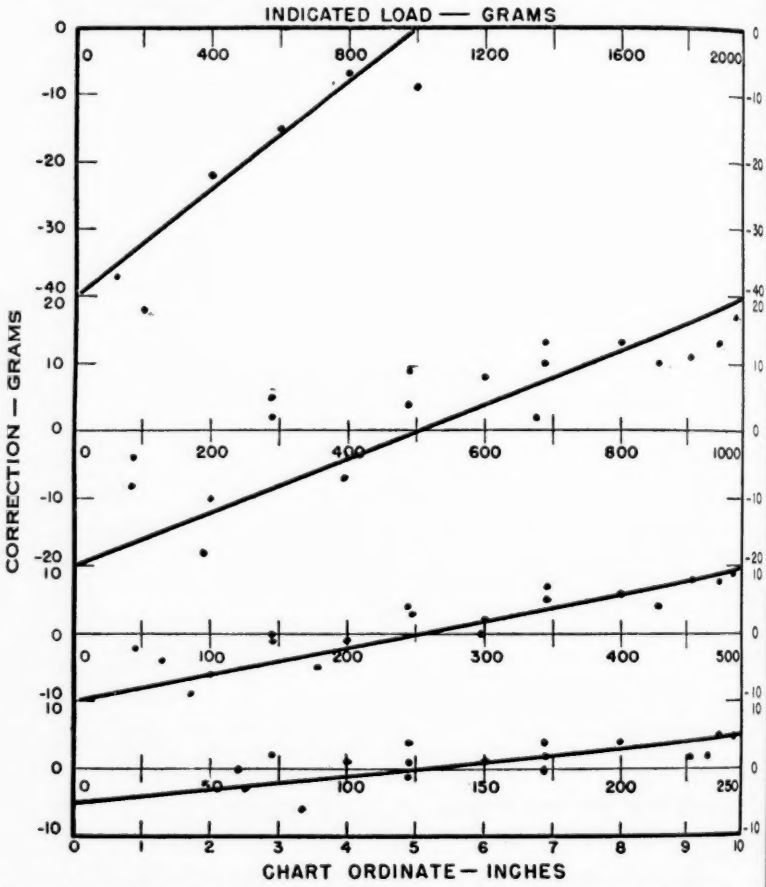

FIGURE 3.—*Calibration correction of the type B machine for 250-, 500-, 1,000-, and 2,000-g capacity.*

change in sin θ, and therefore in the applied load, W sin θ, increases uniformly with time, it readily can be seen from figure 4 that the distance of the cord from D to B does not decrease uniformly with time. Therefore, the motion of the chart is not uniform, and the uniform load scale, ordinate on the chart, will be in error, depending upon the variation in the chart speed. The increase in the chart speed at zero load compared with that at full load was determined and found to be equal to 4.2 percent. The progressive change in the correction for each capacity, amounting to about 4 percent of each capac-

ity, is entirely attributable to the operation of the recording mechanism. If this condition were remedied the correction of this machine for each capacity would be substantially a constant and therefore could be held within a small tolerance by adjusting the weight of the

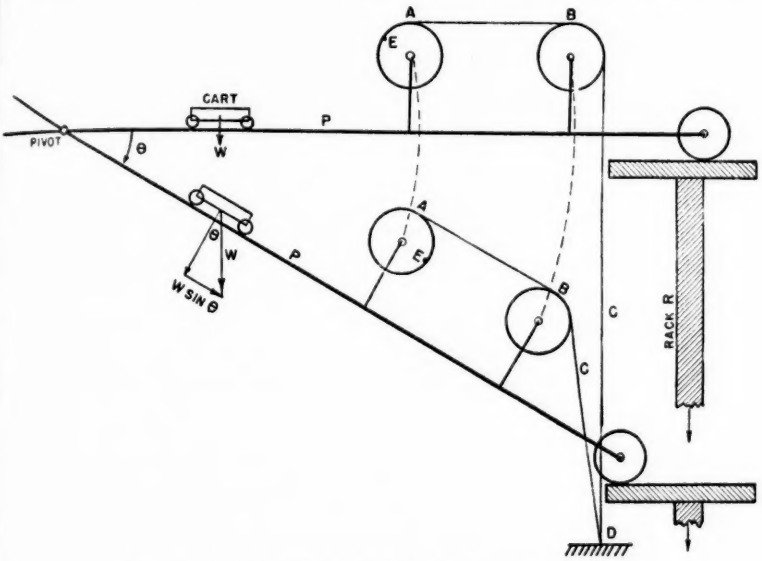

FIGURE 4.—*Schematic drawing of type B machine.*

cart. Table 2 contains the corrections applied in this paper for the type *B* machine.

TABLE 2.—*Calibration corrections for the type B machine*

250-g capacity		500-g capacity		1,000-g capacity		2,000-g capacity	
Indicated load	Correction	Indicated load	Correction	Indicated load	Correction	Indicated load	Correction
g	*g*	*g*	*g*	*g*	*g*	*g*	*g*
0	−5	0	−10	0	−20	0	−40
25	−4	50	−8	100	−16	100	−36
50	−3	100	−6	200	−12	200	−32
75	−2	150	−4	300	−8	300	−28
100	−1	200	−2	400	−4	400	−24
125	0	250	0	500	0	500	−20
150	1	300	2	600	4	600	−16
175	2	350	4	700	8	700	−12
200	3	400	6	800	12	800	−8
225	4	450	8	900	16	900	−4
250	5	500	10	1,000	20	1,000	0

III. MATERIALS, TESTING CONDITIONS, AND RESULTS

The cotton yarns for this investigation were spun on a small experimental spinning frame. Four bobbins of each kind of yarn were received. The nominal yarn numbers and twist multipliers of the yarns tested are listed in table 3.

TABLE 3.—*Results of tests on cotton yarns*

[The asterisk indicates that the difference is significant]

Typp number		Twist multiplier	Testing conditions				Breaking strength, ± standard error						Elongation at rupture, ± standard error	
							Bobbin				Average	Combined average	Average	Combined average
Nominal	Actual		Type of testing machine	Speed of lower jaws	Capacity	Approximate rate of loading	1	2	3	4				
50	51.6	3	*A*	*in./min* 5 12	*g* 500 500	*g/den. min* 7.2 17.2	*g* 162 ±3.9 171 ±4.3	*g* 164 ±4.1 171 ±3.4	*g* 148 ±4.5 153 ±3.9	*g* 174 ±3.8 175 ±4.6	*g* 162 ±2.1 168 ±2.1	*g* 165 ±1.5	% 6.04 ±0.05 6.12 ±0.07	% 6.08 ±0.043
Significance ratio							1.6	1.3	0.8	0.2	2.0		1.0	
50	51.6	3	*B*		250 500	2.8 5.6	160 ±3.8 173 ±3.7	163 ±3.6 179 ±3.4	158 ±4.1 174 ±2.6	174 ±3.4 189 ±2.9	164 ±1.9 179 ±1.6	171 ±1.2	5.73 ±0.05 5.67 ±0.05	5.70 ±0.035
Significance ratio							2.4†	3.2*	3.3*	3.4*	6.0*	3.2*	−0.8	−6.5*
50	54.2	4	*A*	5 12	500 500	7.2 17.2	161 ±6.8 169 ±3.4	170 ±4.3 182 ±4.3	169 ±3.7 185 ±3.6	168 ±5.0 177 ±5.0	167 ±2.6 178 ±2.1	173 ±1.6	6.38 ±0.06 6.71 ±0.07	6.55 ±0.05
Significance ratio							1.1	1.3	3.1*	1.3	3.3*		3.7*	
50	54.2	4	*B*		250 500	2.8 5.6	175 ±5.2 190 ±4.8	183 ±2.8 189 ±3.7	170 ±3.1 191 ±3.8	179 ±5.0 200 ±2.6	177 ±2.1 193 ±2.1	185 ±1.5	6.23 ±0.07 5.78 ±0.07	6.01 ±0.05
Significance ratio							1.9	1.3	4.2*	3.7*	8.0*	5.5*	−4.5*	−8.0*
50	49.6	5	*A*	5 12	500 500	6.4 15.4	185 ±5.5 184 ±6.1	169 ±5.8 173 ±5.7	187 ±6.5 184 ±6.3	172 ±6.4 175 ±5.1	178 ±3.0 179 ±3.0	179 ±2.1	8.15 ±0.09 8.18 ±0.09	8.17 ±0.06
Significance ratio							−0.1	0.5	−0.3	0.3	0.2		0.2	
50	49.6	5	*B*		250 500	2.8 5.6	192 ±5.2 198 ±5.9	172 ±4.0 191 ±5.6	211 ±5.2 201 ±5.0	162 ±6.2 176 ±4.2	184 ±2.6 192 ±2.6	188 ±1.8	7.74 ±0.11 6.93 ±0.10	7.34 ±0.07
Significance ratio							0.8	2.8	−1.4	1.9	2.2	3.2*	−5.4*	−8.5*
50	49.2	6	*A*	5 12	500 500	5.8 13.9	147 ±7.6 171 ±6.0	140 ±5.1 145 ±4.2	137 ±5.8 160 ±4.0	145 ±6.6 157 ±5.0	142 ±3.2 158 ±2.4	150 ±2.0	8.23 ±0.11 8.58 ±0.10	8.41 ±0.07
Significance ratio							2.5	0.8	3.2*	1.5	4.0*		1.7	

50	49.2	6	4	{ 5 / 12	500 / 500	5.8 / 13.9	147 ±7.6 / 171 ±6.0	140 ±5.1 / 145 ±4.2	137 ±5.8 / 160 ±4.0	145 ±6.6 / 157 ±5.0	142 ±3.2 / 158 ±2.4	150 ±2.0	8.23 ±0.11 / 8.58 ±0.10	8.41 ±0.07
Significance ratio							2.5	0.8	3.2*	1.5	4.0*		1.7	
50	49.2	6	*B*		{ 250 / 500	2.8 / 5.6	155 ±3.0 / 169 ±4.1	160 ±2.1 / 171 ±4.6	158 ±5.1 / 175 ±4.4	160 ±6.0 / 172 ±5.2	158 ±2.2 / 172 ±2.4	165 ±1.6	7.65 ±0.11 / 7.05 ±0.11	7.35 ±0.08
Significance ratio							2.8	2.2	2.5	1.5	4.2*	5.8*	−3.8*	−9.8*
25	25.2	3	*A*	{ 5 / 12	500 / 500	3.9 / 9.3	194 ±6.0 / 205 ±6.1	212 ±6.8 / 208 ±4.9	232 ±9.1 / 245 ±6.4	183 ±6.3 / 193 ±8.0	205 ±3.6 / 213 ±3.2	209 ±2.4	5.93 ±0.05 / 6.25 ±0.05	6.09 ±0.04
Significance ratio							1.3	−0.5	1.2	1.0	1.7		4.8*	
25	25.2	3	*B*		{ 500 / 1000	2.8 / 5.6	191 ±5.7 / 214 ±5.6	208 ±4.4 / 212 ±6.1	222 ±4.5 / 240 ±5.1	197 ±4.7 / 223 ±4.3	204 ±2.4 / 222 ±2.6	213 ±1.8	5.76 ±0.06 / 5.73 ±0.04	5.75 ±0.04
Significance ratio							2.9	0.5	2.7	4.2*	5.1*	1.3	−0.4	−4.6*
25	25.5	4	*A*	{ 5 / 12	500 / 500	3.9 / 9.4	229 ±4.5 / 232 ±6.9	259 ±7.1 / 266 ±5.7	246 ±7.2 / 258 ±7.3	206 ±6.1 / 245 ±5.7	235 ±3.2 / 250 ±3.2	242 ±2.3	6.14 ±0.06 / 6.58 ±0.07	6.36 ±0.05
Significance ratio							0.4	0.8	1.2	4.6*	3.3*		4.9*	
25	25.5	4	*B*		{ 500 / 1000	2.8 / 5.6	285 ±6.1 / 268 ±7.7	260 ±6.4 / 264 ±5.8	271 ±6.9 / 262 ±5.6	267 ±7.5 / 261 ±7.8	271 ±3.4 / 264 ±3.4	267 ±2.4	6.29 ±0.07 / 6.18 ±0.07	6.24 ±0.05
Significance ratio							−1.7	0.5	−1.0	−0.6	−1.5	7.6*	−1.1	−1.8
25	25.3	5	*A*	{ 5 / 12	500 / 500	3.8 / 9.2	261 ±4.9 / 242 ±7.2	245 ±6.8 / 270 ±7.8	241 ±6.2 / 269 ±5.3	247 ±7.5 / 281 ±7.5	248 ±3.2 / 266 ±3.5	257 ±2.4	6.95 ±0.08 / 7.40 ±0.10	7.18 ±0.06
Significance ratio							−2.2	2.4	3.4*	3.2*	3.8*		3.5*	
25	25.3	5	*B*		{ 500 / 1000	2.8 / 5.6	267 ±7.0 / 287 ±7.2	275 ±6.7 / 282 ±6.8	267 ±6.6 / 293 ±6.1	280 ±5.3 / 278 ±8.0	272 ±3.2 / 285 ±3.5	278 ±2.4	7.32 ±0.09 / 7.49 ±0.09	7.41 ±0.6
Significance ratio							2.0	0.7	2.9	−0.2	2.8	6.2*	1.3	2.7
25	24.6	6	*A*	{ 5 / 12	500 / 500	3.5 / 8.4	241 ±7.4 / 252 ±6.5	240 ±6.8 / 242 ±7.5	258 ±7.9 / 224 ±6.4	252 ±6.6 / 250 ±6.2	248 ±3.6 / 242 ±3.3	245 ±2.4	8.48 ±0.10 / 8.24 ±0.11	8.36 ±0.07
Significance ratio							1.1	0.2	−3.4*	−0.2	−1.2		−1.6	
25	24.6	6	*B*		{ 500 / 1000	2.8 / 5.6	258 ±6.9 / 267 ±6.1	258 ±7.3 / 276 ±7.5	273 ±8.2 / 270 ±7.1	277 ±5.5 / 299 ±7.1	267 ±3.5 / 278 ±3.5	273 ±2.5	8.10 ±0.10 / 8.29 ±0.11	8.20 ±0.07
Significance ratio							1.0	1.7	−0.3	2.4	1.8	8.0*	1.3	−1.5

TABLE 3.—*Results of tests on cotton yarns*—Continued

Typp number		Twist multiplier	Testing conditions				Breaking strength, ± standard error						Elongation at rupture, ± standard error	
							Bobbin				Average	Combined average	Average	Combined average
Nominal	Actual		Type of testing machine	Speed of lower jaws	Capacity	Approximate rate of loading	1	2	3	4				
12.5	12.1	3	*A*	*in./min* 5 12	*g* 2000 2000	*g/den. min.* 4.6 11.0	*g* 493 ±9.0 489 ±6.9	*g* 420 ±5.9 410 ±6.5	*g* 454±12.0 440 ±6.9	*g* 431 ±8.7 450 ±9.8	*g* 450 ±4.6 447 ±3.8	*g* 448 ±3.0	% 7.76 ±0.04 7.84 ±0.07	% 7.80 ±0.04
Significance ratio							−0.4	−1.1	−1.0	1.5	−0.5		1.0	
12.5	12.1	3	*B*		1000 2000	2.8 5.6	500 ±9.2 557 ±6.9	463 ±8.7 511 ±9.0	439 ±9.1 470 ±4.6	481 ±9.9 549 ±10.8	471±4.6 522±4.1	496 ±3.1	7.51 ±0.05 7.60 ±0.04	7.56 ±0.03
Significance ratio							5.0*	3.8*	3.0*	4.7*	8.2*	11.1*	1.7	−4.3*
12.5	11.8	4	*A*	5 12	2000 2000	4.8 11.5	602 ±11.1 592 ±11.8	585 ±11.2 572 ±11.1	632 ±11.0 577 ±11.9	566 ±9.4 580 ±6.5	596 ±5.4 580 ±5.3	588 ±3.8	8.99 ±0.06 9.55 ±0.07	9.27 ±0.05
Significance ratio							−0.6	−0.8	−3.4*	1.2	−2.1		6.2*	
12.5	11.8	4	*B*		1000 2000	2.8 5.6	627 ±12.0 693 ±8.3	585 ±11.2 639 ±6.7	603 ±6.8 641 ±10.9	596 ±8.6 636 ±8.4	603 ±4.9 652 ±4.4	628 ±3.3	9.50 ±0.06 9.40 ±0.05	9.45 ±0.04
Significance ratio							4.5*	4.2*	3.0*	3.3*	7.4*	8.0*	−1.3	3.0*
12.5	12.2	5	*A*	5 12	2000 2000	4.7 11.4	547 ±9.3 592 ±12.2	608 ±9.2 590 ±10.4	587 ±10.2 596 ±12.5	595 ±11.9 596 ±12.1	584 ±5.1 594 ±5.9	589 ±3.9	9.38 ±0.07 9.90 ±0.07	9.64 ±0.05
Significance ratio							2.9	−1.3	0.5	0.1	1.3		5.2*	
12.5	12.2	5	*B*		1000 2000	2.8 5.6	598 ±8.3 615 ±11.8	585 ±8.3 607 ±11.0	599 ±11.0 626 ±15.3	619 ±9.6 627 ±10.5	600 ±4.7 619 ±6.2	609 ±3.9	9.59 ±0.06 9.28 ±0.08	9.44 ±0.05
Significance ratio							1.2	1.6	1.4	0.6	2.4	3.6*	−3.1*	−2.9

12.5	12.2	6	*A*	5 12	2000 2000	4.2 10.1	505 ±12.0 548 ±13.7	533 ±11.7 560 ±11.1	511 ±10.1 535 ±12.4	547 ±11.2 553 ±9.8	524 ±5.6 549 ±5.9	536 ±4.0	10.35 ±0.06 10.64 ±0.10	10.49 ±0.07
Significance ratio							2.4	1.7	1.5	0.4	3.1*		2.3	

12.5	12.2	6	A	5 12	2000 2000	4.2 10.1	505 ±12.0 548 ±13.7	533 ±11.7 560 ±11.1	511 ±10.1 535 ±12.4	547 ±11.2 553 ±9.8	524 ±5.6 549 ±5.9	536 ±4.0	10.33 ±0.09 10.64 ±0.10	10.49 ±0.07
Significance ratio							2.4	1.7	1.5	0.4	3.1*		2.3	
12.5	12.2	6	B		1000 2000	2.8 5.6	528 ±12.2 577 ±10.2	544 ±8.0 550 ±15.3	524 ±8.0 539 ±11.0	550 ±9.7 553 ±17.1	536 ±4.8 555 ±6.9	545 ±4.2	10.04 ±0.11 9.99 ±0.11	10.02 ±0.08
Significance ratio							3.1*	0.4	1.1	0.2	2.3	1.6	−0.3	−4.6*
6.25	6.22	3	A	5 12	2000 2000	2.9 7.0	793 ±20.2 739 ±27.8	706 ±17.0 748 ±17.1	955 ±29.9 923 ±31.2	809 ±25.4 863 ±25.0	816 ±11.8 818 ±12.9	817 ±8.7	8.06 ±0.06 7.96 ±0.06	8.01 ±0.04
Significance ratio							−1.6	1.7	−0.7	1.5	0.1		−1.2	
6.25	6.50	4	A	5 12	2000 2000	3.0 7.2	1237 ±20.8 1167 ±17.2	1033 ±18.8 1042 ±18.2	1112 ±18.1 1260 ±17.5	1070 ±17.2 1201 ±16.5	1113 ± 9.4 1168 ± 8.7	1140 ±6.4	9.84 ±0.09 9.70 ±0.06	9.77 ±0.05
Significance ratio							−2.6	0.3	5.9*	5.4*	4.3*		−1.3	
6.25	6.15	5	A	5 12	2000 2000	3.0 7.0	1266 ±26.7 1265 ±26.9	1251 ±20.9 1272 ±19.4	1050 ±30.6 1262 ±23.7	1088 ±29.0 1201 ±25.7	1164 ±13.5 1250 ±12.1	1207 ±9.1	10.91 ±0.12 11.74 ±0.11	11.33 ±0.08
Significance ratio							0	0.7	5.5*	2.9	4.7*		5.1*	
6.25	5.92	6	A	5 12	2000 2000	2.5 6.0	1193 ±22.6 1315 ±26.6	989 ±27.6 984 ±23.7	1203 ±27.0 1201 ±22.5	922 ±25.2 1092 ±25.3	1077 ±12.8 1148 ±12.3	1112 ±8.9	14.46 ±0.23 15.10 ±0.22	14.78 ±0.16
Significance ratio							3.5*	−0.1	0	4.7*	4.0*		2.0	

The yarns were conditioned for several days in an atmosphere of 65-percent relative humidity and 70° F and were tested in this atmosphere. The test specimens were mounted between two pairs of flat jaws spaced 10 inches apart. Before clamping the yarn in the second pair of jaws, a tension of 5 g was applied by the use of a suitable weight. Twenty-five breaks were made for the yarn on each bobbin for each of the testing conditions used. The various testing conditions, including type of machine, capacity of machine, speed of pulling jaws for the type *A* machine, and the approximate rate of loading expressed in grams per denier per minute are listed in table 3.[4]

The averages of the 25 breaks determined for the yarn on each bobbin, hereafter called the breaking strengths of the bobbins, for each of the testing conditions used are given in table 3, together with the standard error of each average. These values have been corrected, using the applicable corrections of the testing machines. The results of tests in which the specimen ruptured near either pair of jaws were not discarded. The number of ruptures near either pair of jaws was less than 5 percent, and the magnitudes of these ruptures were consistently as high as ruptures further removed from the jaws. Table 3 also contains, for each testing condition, the average breaking strength and the average elongation at rupture of each yarn (average of the results for the four bobbins), together with their respective standard errors. Finally, significance ratios (difference of two values divided by the standard error of the difference) are given directly below the pair of values chosen for comparison. In the following discussion a significance ratio numerically equal to 3 or more is considered to show a significant difference between any two values which are compared. A significance ratio less than 3 indicates either that the two values do not differ significantly or that the number of tests were insufficient to detect a significant difference.

IV. DISCUSSION OF RESULTS

1. VARIATION IN BREAKING STRENGTH OF COTTON YARN

The variation in breaking strength of a cotton yarn includes the variation in breaking strength of the yarn on each bobbin, hereafter called the variation within bobbins, and the variation of the yarn between bobbins of the same kind of yarn, hereafter called the variation between bobbins. These variations are expressed on a comparable basis for the different yarns by the coefficient of variation. The average coefficients of variation of breaking strength within bobbins on the type *A* machine are 12.9 and 11.9 percent for the speeds of the lower jaws equal to 5 and 12 inches per minute, respectively. The difference between these two values is not significant, the significance ratio being only 1.5. The average coefficients of

[4] The rate of loading for type *A* machine is not constant throughout the test. It depends upon the characteristics of the machine, that is, capacity of machine and movement of upper jaws per unit load, and upon the elongation of the specimen per unit load. The values reported in this paper for the type *A* machine were computed as follows: The movement of the upper jaws, which corresponds to an indicated load equal to the breaking strength of a specimen, plus the elongation at rupture of the specimen is equal to the movement of the lower jaws in inches. This value divided by the speed of the lower jaws equals the time to rupture the specimen. The breaking load in grams divided by this time in minutes gives the rate of loading of the specimen in grams per minute. Dividing this value by the denier of the specimen converts the rate of loading to the unit used in table 3.

variation of breaking strength within bobbins on the type *B* machine are 11.0 and 10.6 percent for the low and high rates of loading, respectively. These two values do not differ significantly, the significance ratio being 0.6. However, the difference between these coefficients of variation for machines *A* and *B*, amounting to 14 percent, is significant, the significance ratio being 3.5 This difference of 14 percent in the variability of the breaking strength obtained on the two machines will be reflected in the results discussed in section 2, below.

The variation in breaking strength between bobbins of a given yarn may constitute a considerable portion of the variation of the yarn. It is apparent from the results given in table 3 that for some yarns the breaking strengths of the bobbins may differ significantly. The significance ratios of breaking strength between the possible combinations of pairs of bobbins for each yarn were computed. It was found that approximately 30 percent of these pairs had a significance ratio greater than 3 and, therefore, differed significantly.

2. EFFECT OF RATE OF LOADING ON BREAKING STRENGTH AND ELONGATION

The effect of rate of loading on the breaking strength and elongation of cotton yarns is shown by the data given in table 3. The following facts are based upon a critical study of these data.

When the rate of loading of the type *A* machine was increased by increasing the speed of the lower jaws from 5 to 12 inches per minute, 15 percent of the bobbins tested showed a significant increase in the breaking strength and 55 percent showed an increase which was not significant. Of the remaining bobbins, 27 percent showed a decrease which was not significant, and 3 percent showed a significant decrease in breaking strength.

When the rate of loading of the type *B* machine was increased from about 2.8 to 5.6 g per denier per minute, 31 percent of the bobbins tested showed a significant increase in the breaking strength and 56 percent showed an increase which was not significant. The remaining bobbins, 13 percent, showed a decrease in breaking strength which was not significant.

When the rate of loading of the type *A* machine was increased by increasing the speed of the lower jaws from 5 to 12 inches per minute, 50 percent of the yarns tested showed a significant increase in breaking strength and 31 percent showed an increase which was not significant. The remaining yarns, 19 percent, showed a decrease in breaking strength which was not significant.

When the rate of loading of the type *B* machine was increased from about 2.8 to 5.6 g per denier per minute, 50 percent of the yarns tested showed a significant increase in the breaking strength and 42 percent showed an increase which was not significant. The remaining yarns, 8 percent, showed a decrease in breaking strength which was not significant.

The over-all effect of increasing the rate of loading of the type *A* machine by increasing the speed of the lower jaws from 5 to 12 inches per minute was an increase of 3.8 percent in the breaking strength. This increase is highly significant, the significance ratio being 7.8.

The over-all effect of increasing the rate of loading of the type *B* machine from about 2.8 to 5.6 g per denier per minute was an increase

of 5.8 percent in the breaking strength. This increase is highly significant, the significance ratio being 12.3.

The breaking strength of the cotton yarns tested on the type *B* machine at the two rates of loading was 6.1 percent higher than the breaking strength of the same yarns when tested on the type *A* machine at the two speeds of the lower jaws. This difference was highly significant, the significance ratio being 18.0. This result was not expected, and it cannot be explained as an effect due to a difference in the rate of loading, since the average rate of loading for the type *A* machine, namely, 8.5 g per denier per minute, is approximately twice the average rate of loading of the type *B* machine, which is only about 4.2 g per denier per minute.

The effect of rate of loading on the breaking strength of the bobbins and the yarns is brought out more decisively on the type *B* machine than on the type *A* machine. This difference in the effect of rate of loading may result in part because of the difference in variability of the breaking strength obtained on the two machines.

When the rate of loading of the type *A* machine was increased by increasing the speed of the lower jaws from 5 to 12 inches per minute, 54 percent of the yarns tested showed a significant increase in the elongation, and 37 percent showed an increase which was not significant. The remaining yarns, 19 percent, showed a decrease in elongation which was not significant. The over-all effect of increasing the rate of loading on the type *A* machine was an increase of 3.3 percent in the elongation. This difference was highly significant, the significance ratio being 8.1. This effect was opposite to that expected from an increase in the rate of loading.

When the rate of loading of the type *B* machine was increased from about 2.8 to 5.6 g per denier per minute, 33 percent of the yarns tested showed a significant decrease in the elongation and 42 percent showed a decrease which was not significant. The remaining yarns, 25 percent, showed an increase which was not significant. The over-all effect of increasing the rate of loading of the type *B* machine was a decrease of 2.3 percent in the elongation. This difference was significant, the significance ratio being 5.2. This effect was in accordance with that expected from an increase in the rate of loading.

The elongation at rupture of the cotton yarns tested on the type *B* machine at the two rates of loading was 4.2 percent lower than the elongation of the same yarns when tested on the type *A* machine for the two speeds of the lower jaws. This difference was highly significant, the significance ratio being 14.0. This result and also the result that an increase in the rate of loading on the two types of machine produced opposite effects on the elongation were not expected. Further consideration is being given to these and the other unexpected results mentioned above.

Finally, an analysis of variance indicated that the effect of rate of loading on the breaking strength and the elongation, on either type of machine, did not vary significantly with either the yarn size or with the twist multiplier.

The over-all effects of the rate of loading and of the type of machine on the breaking strength and the elongation, based upon the average breaking strength and average elongation of the 50s, 25s, and 12.5s cotton yarns, are summarized in table 4. These values are plotted in

figure 5 against the logarithm of the rate of loading, the size of the dot being equal to the standard error. Castricum and Benson [5] found that the equation

$$S = S_1 + KS_1 \log R$$

gives a better representation of the relation between the rate of loading, R, and the breaking strength, S, than the linear function suggested by Bellinson.[6] In this equation, K is a constant and S_1

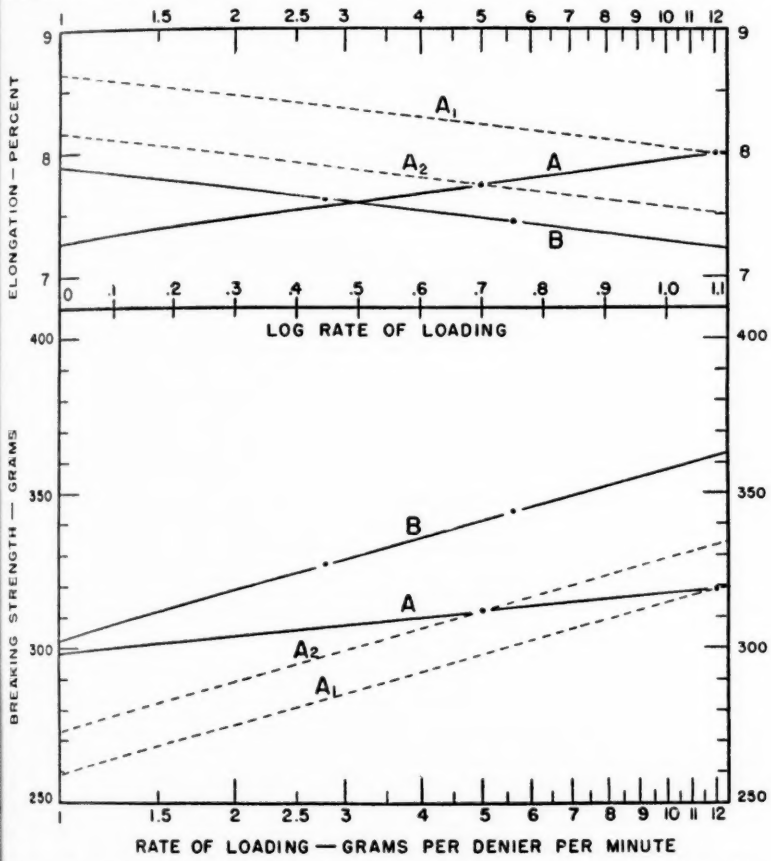

FIGURE 5.—*Curves showing the effect of rate of loading and type of testing machine on the breaking strength and elongation of cotton yarns.*

The broken lines represent the curves which should be obtained on the type *A* machine for the two conditions of operation, if it is assumed that the type *B* machine gives more nearly the correct effect of the rate of loading on the breaking strength and elongation of cotton yarns.

equals the breaking strength when R is unity. By using the solid curves, the effect of the same change in the rate of loading can be compared for the two types of machine. One would expect that a given change in the rate of loading for either machine would produce

[5] *The effect of rate of loading on tensile strength of cord and yarn.* ASTM Preprint (June 1941).
[6] *Viscose rayon: Stress-strain properties. II. Effect of rate of load,* Textile Research, **10**, 316-322 (June 1940).

the same effect on the breaking strength and elongation. The same effect is obviously not obtained for the two machines.

TABLE 4.—*Average breaking strength and average elongation based upon all of the tests on the 50s, 25s, and 12.5s cotton yarns*

Type of machine	Average rate of loading	Number of tests	Breaking strength		Elongation	
			Average	Standard error	Average	Standard error
	g/den./min		*g*	*g*	*Percent*	*Percent*
A	[a] 5	1,200	312	1.13	7.73	0.022
A	[b] 12	1,200	319	1.11	8.00	.025
B	2.8	1,200	327	1.01	7.63	.024
B	5.6	1,200	344	1.13	7.45	.026

[a] The values which gave this average ranged from 3.5 to 7.2.
[b] The values which gave this average ranged from 8.4 to 17.2.

However, if it is assumed that the type *B* machine gives more nearly the correct effect of the rate of loading on the breaking strength and the elongation, then the broken lines represent the curves which should be obtained on the type *A* machine for the two conditions of operation, that is, with and without the use of the auxiliary pulley. On this assumption, the differences between curves *B* and A_1 and between *B* and A_2 are attributed to conditions which are believed to exist primarily in the type *A* machine. The differences between curves A_1 and A_2 for breaking strength and for elongation may be attributed to factors associated with the auxiliary pulley, which was mounted on a separate base and detached from the frame of the machine. The effects of a number of factors which may contribute to these differences are being considered.

3. EFFECT OF TWIST MULTIPLIER ON BREAKING STRENGTH AND ELONGATION

The effect of twist multiplier on the breaking strength and the elongation of the cotton yarns tested is shown in figure 6, where the average strength and average elongation of all the tests on each yarn are plotted against the twist multiplier. Previous conclusions, namely, that the breaking strength of a cotton yarn increases with twist multiplier to a maximum and then decreases for higher twist multipliers and that the elongation increases with twist multiplier, are confirmed.

4. COEFFICIENT OF VARIATION OF COTTON YARNS OF VARIOUS TYPP NUMBERS AND TWIST MULTIPLIERS

Table 5 contains the coefficients of variation of breaking strength and of elongation of the various cotton yarns tested on the two types of machines. The general observation that the coefficient of variation of breaking strength is a minimum at the twist multiplier giving maximum strength confirms the results of our tests on cotton yarns of 8.4s and 67s typp number.[7] The coefficient of variation is also

[7] Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns*, J. Research NBS 15, 237–253 (1935) RP826.

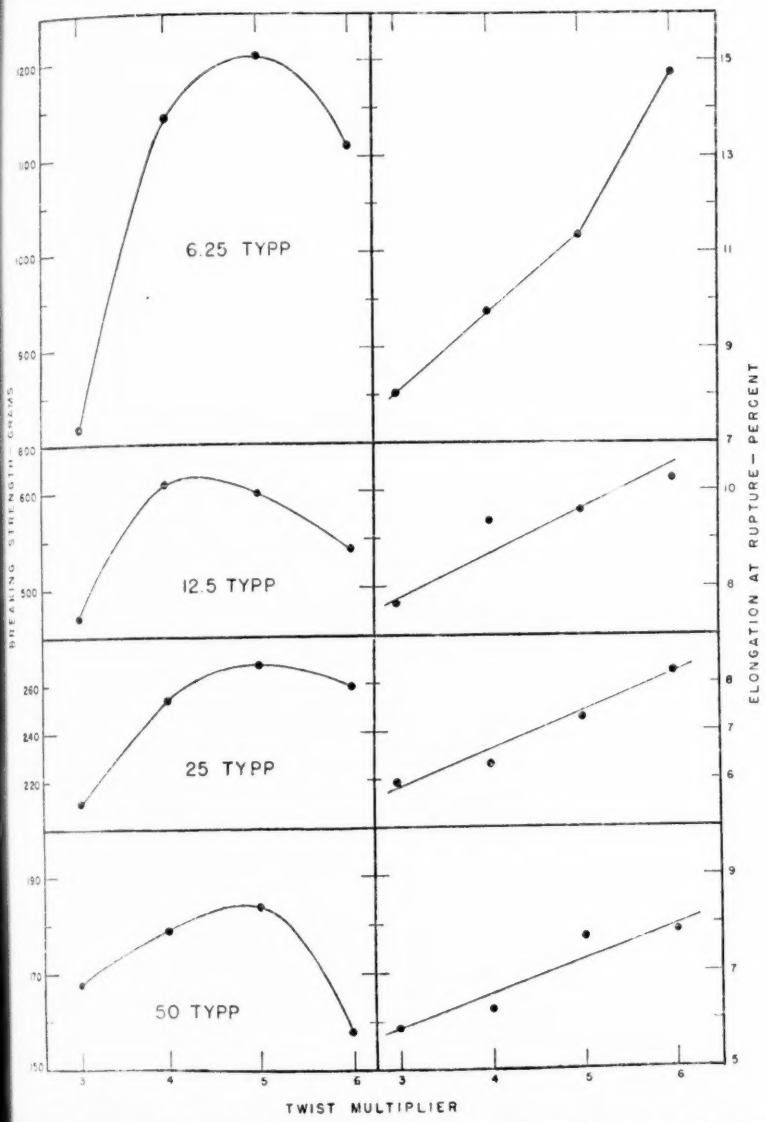

FIGURE 6.—*Effect of twist multiplier on breaking strength and elongation of cotton yarns.*

seen to vary with the typp number. The 12.5s yarn had a significantly lower coefficient of variation than the other yarns for both breaking strength and elongation. The average coefficient of variation of breaking strength on the type *A* machine was about 14 percent higher than the value for the same yarns when tested on the type *B* machine. This difference is significant. The coefficient of variation of elongation on the type *A* machine is about 7 percent lower than the value for the same yarns when tested on the type *B* machine.

TABLE 5.—*Coefficient of variation, V, of breaking strength and elongation of cotton yarns of various typp numbers and twist multipliers for types A and B testing machines*

Type of machine	Typp number	Coefficient of variation, V (percent)									
		For breaking strength					For elongation				
		Twist multiplier				Average	Twist multiplier				Average
		3	4	5	6		3	4	5	6	
A	6.25	17.7	10.4	12.1	14.8	13.8	7.7	7.8	10.4	15.3	10.3
	12.5	11.1	9.3	9.5	11.3	10.3	7.3	7.1	7.5	8.6	7.6
	25	17.5	14.1	13.0	14.0	14.7	8.7	8.7	12.0	11.7	10.0
	50	12.3	12.3	16.9	17.7	14.8	9.5	9.5	11.2	12.1	10.7
Average		14.7	11.5	12.9	14.5	13.4	8.3	8.3	10.3	11.9	9.8
B	12.5	10.1	7.9	8.9	10.8	9.4	5.9	5.7	7.4	10.7	7.4
	25	12.1	12.4	11.9	13.0	12.4	9.1	11.0	11.7	12.9	11.2
	50	10.6	11.5	15.8	15.1	13.5	9.1	11.1	11.1	15.2	12.7
Average		10.9	10.6	12.2	13.0	11.7	8.0	9.3	11.2	12.9	10.6

5. NUMBER OF TESTS CORRESPONDING TO A GIVEN PRECISION AND PROBABILITY

Table 6 contains information regarding the coefficient of variation, V, of breaking strength and of elongation of cotton yarns which can be used as a basis for computing the number of single-strand tests, n, that are required to yield a result which will be in error by not more than $\pm E$ percent for a given probability, P. The values of n may be computed by using the formula $n=t^2V^2/E^2$, where t has the values of 1.645, 1.960, and 2.576 for the probabilities of 0.90, 0.95, and 0.99, respectively. The values of n given in table 6 are for an error of the mean, E, equal to ± 3 percent. In general, if 100 single-strand breaking-strength tests are made on cotton yarns, the chances are 19 out of 20 that the average breaking strength so determined will be in error by less than ± 3 percent.

TABLE 6.—*Coefficients of variation, V, and number of single-strand tests, n, required to yield a result for cotton yarns which will be in error by not more than ±3 percent for the given probability*

Typp number	Type of machine	N[b]	Computed values of n for cotton yarns							
			Breaking strength				Elongation			
			V	Probability			V	Probability		
				0.90	0.95	0.99		0.90	0.95	0.99
			Percent				*Percent*			
6.25	*A*	800	13.8	58	82	140	10.3	32	46	78
12.5	*A*	800	10.3	32	46	78	7.6	18	25	44
12.5	*B*	800	9.4	27	38	64	7.4	17	24	40
25	*A*	800	14.7	66	94	160	10.6	35	48	82
25	*B*	800	12.4	47	67	114	11.2	37	54	92
50	*A*	800	14.8	67	95	160	10.7	35	50	104
50	*B*	800	13.5	56	79	135	12.7	50	70	120
8.4 [a]	*A*	1200	13.8	58	82	140	8.5	22	32	52
67 [a]	*A*	2000	14.7	66	94	160	9.2	26	37	62
2/134 [a]	*A*	1200	15.7	76	107	180				
Average			13.3	55	76	130	9.8	29	42	70

[a] Values of V taken from NBS Research Paper RP826, referred to in footnote 7. The 2/134 is a mercerized yarn of high commercial quality being spun from 1¾-inch staple Sea Island cotton.

[b] N represents the number of single-strand tests upon which the value of V is based.

WASHINGTON, July 9, 1941.

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1.0000 to 2.5000	.0001	15
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